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ON THE ANNUAL AND DIURNAL VARIATION OF THE EVAPORATION FROM THE OCEANS*

By

H. U. SVERDRUP

Scripps Institution of Oceanography
University of California
La Jolla, California

The average annual evaporation of the oceans in different latitudes can be considered fairly well established (Mosby, 1936, Wüst, 1936), but so far little is known as to the character of the annual and the diurnal variations. Helland-Hansen (1930) has pointed out that evaporation will be facilitated if the sea surface is warmer than the air, whereas evaporation will decrease or cease if the sea surface is colder. He has therefore concluded that in middle latitudes the evaporation is at a maximum in fall and early winter, and at a minimum in summer, and, similarly, it may be concluded that the evaporation is at a maximum during the night and is somewhat smaller in the middle of the day. It will here be attempted to approach the problem on the basis of energy considerations which have been applied successfully in the study of the average evaporation from the sea (W. Schmidt, 1915), and of the evaporation from reservoirs and lakes (Ångström, 1920, Cummings and Richardson, 1927). A few specific examples will be discussed and a few conclusions will be drawn.

In this case, the energy equation states that the total amount of heat lost from a square unit of surface area in unit time, q_a, partly

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as heat used for evaporation, q_e, and partly as sensible heat given off to the atmosphere, q_c, must equal the difference between the surplus radiation (radiation from sun and sky minus effective back radiation from the sea surface) which is absorbed by the water, q_r, and the time change of the heat content of the water:

$$q_e + q_c = q_r - \int_0^\infty \frac{d}{dt}(c\rho\tau)\, dz \tag{1}$$

Here c, ϱ, and τ mean specific heat, density and temperature, respectively. The amount of heat given off to the atmosphere by convection is generally assumed to be a small fraction of q_e, and $q_a = q_e + q_c$ represents, therefore, approximately the amount of heat used for evaporation.

The surplus of radiation can be found either by means of Kimball's data (1928) or Mosby's formula (1936), taking into account reflection at the surface and using Ångström's results (1920) as to the effective back radiation. Evaluation of the integral

$$\int_0^\infty \frac{d}{dt}(c\rho\tau)dz = c\rho\left[\int_0^\infty \frac{\partial\tau}{\partial t}dz + \int_0^\infty v_x\frac{\partial\tau}{\partial x}dz + \int_0^\infty v_y\frac{\partial\tau}{\partial y}dz + \int_0^\infty v_z\frac{\partial\tau}{\partial z}dz\right] \tag{2}$$

is generally more difficult, because it necessitates knowledge of the temperature changes within a given water mass. In certain instances approximately correct values can be determined.

ANNUAL VARIATION OF EVAPORATION

Helland-Hansen (1930) has pointed out that water masses of different origin may be carried into the area under examination, for which reason the observed temperature changes may be related to variations in the character of the water masses present and not to processes of heating or cooling. In order to overcome this difficulty, Helland-Hansen examined the "temperature anomalies" as defined by means of deviations from standard T-S curves, and on this basis he arrived at a series of curves showing the effect of heating in three areas of the eastern North Atlantic, the data being relatively complete for an area off the Bay of Biscay, with its center at 47° N. and 12° W. The data are from a region without very distinct currents, for which reason only the first term on the right-hand side of equation (2) has to be considered, and this can be computed from Helland-Hansen's data, introducing $c = 0.93$ and $\varrho = 1.025$. Thus, the curve marked q_τ in Figure 31A was obtained, showing the variation during the year of the

amount of heat involved in heating or cooling the water, and expressed in gm. cal./cm.^{2} min. Kimball gives values of the total incoming radiation on the 21st of every month of the year at 48° N., 4° W., and the effective back radiation in this locality can be obtained by means of Ångström's table using the same values of cloudiness which were used by Kimball in his computation. Thus, the curve marked q_r

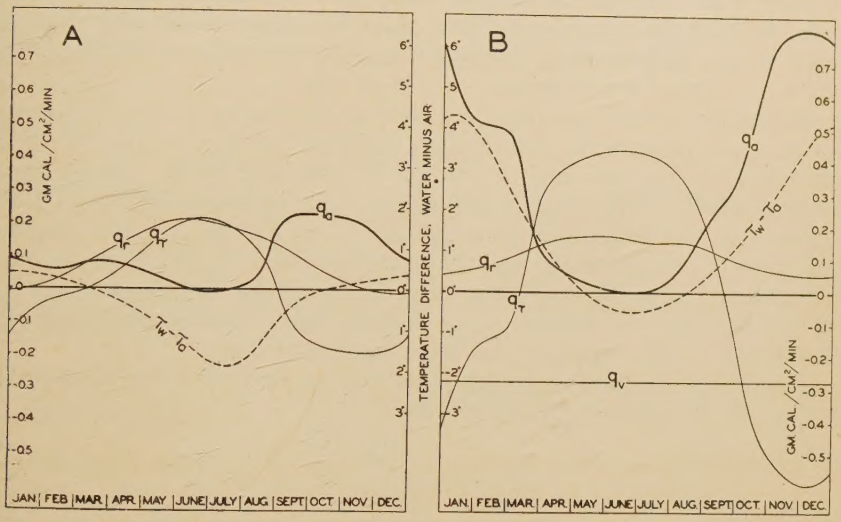

Figure 31. A. Annual variation of evaporation off the Bay of Biscay, in about 47° N. and 12° W. Curve q_r represents the surplus of radiation heat which is absorbed by the water, curve q_T represents the heat involved in heating and cooling the water. Curve q_a represents the heat given off to the atmosphere mainly by processes of evaporation. The curve $\tau_w - \tau_a$ represents the difference between the surface temperature of the water and the temperature of the air. B. Annual variation of evaporation within the region of the Kurosio in about 32° 40′ N. and 135° 50′ E. The designation of the curves is the same as in figure 32 A. In addition, q_v represents the loss of heat of the water due to change of temperature in the direction of flow.

is found showing the variations through the year of the radiation surplus, also expressed in gm. cal./cm.^{2}min. Assuming that the values of q_r are applicable to the same region as those of q_T, the amount of heat given off by evaporation and convection is found by subtraction of the two curves and is represented by curve q_a in Figure 31A.

The curve q_a represents roughly the annual variation of evaporation, and this computation leads therefore to the result that the evaporation is great from the middle of September to the middle of December, is small from January to May, and ceases in June and July. It is of particular interest to observe that a secondary minimum of evaporation appears to occur in February and that apparently the

increase of radiation surplus in early spring is accompanied by an increase in evaporation leading to a secondary maximum in March.

In the figure, the curve marked $\tau_w - \tau_a$ represents the temperature difference between the water and the air as derived from the charts for seasons in the Atlas of Climatological Charts (1939). The agreement between this curve and the curve q_a is good, as should be expected from Helland-Hansen's reasoning. Assuming that in this case 90% of the total heat loss is used for evaporation, one obtains that in late fall the daily evaporation amounts to about 0.5 cm. and the total annual evaporation to about 81 cm.

A similar method has been applied to the region south of Japan, using data concerning the annual variation of temperature in the waters of the Kurosio in about 32° 40′ N. and 135° 50′ E. At stations located along a line running due south from Siono-misaki, about 100 miles long and extending from 33° 30′ N. to 31° 50′ N., the annual variation of temperature was examined by Suda on the basis of observations from 1923 to 1927. The observations which were taken in the N.E.-flowing branch of the Kurosio have been re-examined by Koenuma (1939), whose tables have been used here.

The radiation income in this area can be derived from Kimball's data. If, in this case, one introduces

$$q_\tau = c\rho \int_0^\infty \frac{\partial \tau}{\partial t} dz$$

one arrives at the result that in summer large amounts of heat are taken up from the atmosphere. This appears unreasonable and must be due to the fact that the other terms in (2) can not be neglected, because in this region a distinct current exists within which the temperature decreases in the direction of flow. It is not known how great this decrease is, nor whether it is independent of the seasons, but for the sake of simplicity it will be assumed that the term

$$q_v = c\rho \int_0^\infty v_x \frac{\partial \tau}{\partial x} dz$$

is constant throughout the year and so great that in summer q_a becomes zero and that other terms can be omitted. Figure 32B shows the curves q_r, q_τ, and q_v, and

$$q_a = q_r - q_\tau - q_v$$

which approximately represents the evaporation. In this case the evaporation is at a maximum in winter, and this result appears trust-

worthy, because in winter the cold and dry monsoon blows from the Asiatic Continent.

In November, December, and January an average of .750 gm. cal./cm.^{2} min. is given off to the atmosphere. Of this amount three-fourths or more is given off as latent heat of water vapor corresponding to an evaporation of about 1.4 cm. per day. On a similar basis the total evaporation in one year would amount to 266 cm. which is more than twice Wüst's average value in that latitude, 116 cm. per year. The difference indicates that the evaporation is greatest near the west-

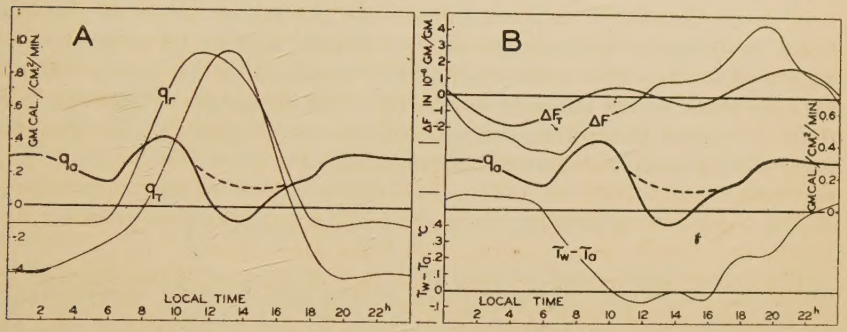

Figure 32. A. Diurnal variation of evaporation in the tropics, according to observations on four "Meteor" stations. The designation of the curves is the same as in figure 32A. B. The curve q_a represents the diurnal variation of heat given off to the atmosphere at four "Meteor" stations, the curves $\tau_w - \tau_a$ and ΔF represent the difference between water-surface temperature and air temperature, and the diurnal variation of the specific humidity of the air on the same four days. The curve ΔF_T represents the diurnal variation of the specific humidity of the air on 18 selected days in the tropics, according to Reger.

ern border of the North Pacific Ocean, as may be expected when the character of the currents and the atmospheric circulation is considered.

The temperature difference, water minus air, which is also shown in the figure as derived from the Atlas of Climatological Charts of the Oceans, varies as the computed evaporation and in winter is greater near Japan than anywhere else in the Pacific Ocean.

In the part of the Kurosio under consideration, one may perhaps assume that the velocity between the surface and 200 meters is 50 cm./sec. With this value of v one finds that the value of q_v which was introduced corresponds to a decrease of the temperature of 0.2° C. in the upper 200 meters on a distance of about 400 km. It is impossible to verify this conclusion because the change in temperature in the direction of flow of the Kurosio appears to be mainly caused by admixture of colder water. The estimated cooling due to the

amount of heat given off to the atmosphere appears, however, to be conservative.

DIURNAL VARIATION OF EVAPORATION IN THE TROPICS

In order to examine the diurnal variation of evaporation by means of the same method it is necessary to know the diurnal variation of temperature at different depths. From the tropics the observations at four of the "Meteor" anchor stations give the necessary information. These data have been examined by Defant (1932) who, from the decrease of amplitude and change of phase of the diurnal variation of temperature at the surface and at 50 meters, concluded that the eddy conductivity was constant in the upper homogeneous layer which had a thickness of about 70 meters. This implies that the diurnal variation of temperature at a depth z can be expressed by means of a sum of harmonic terms,

$$\tau = \Sigma A_n e^{-\varkappa_n z} \sin\left(n\frac{2\pi}{T}t + \alpha_n - \varkappa_n z\right)$$

where A_n represents the amplitude of the nth term at the surface, α_n, the phase of that term at the surface, T, the length of the day in hours, minutes, or seconds depending upon the units used for measuring the time, and where

$$\varkappa_n = \sqrt{\frac{n\pi\rho}{\eta T}}$$

Here, η is the eddy conductivity. From change of phase and reduction of amplitude Defant found $\eta = 322$ gm./cm. sec. The amount of heat used in unit time for local heating and cooling is, therefore,

$$q_\tau = c\rho\int_0^\infty \frac{\partial t}{\partial t}\,dz = \Sigma A_n \frac{n2\pi}{T}\frac{c\rho}{\varkappa_n 2\sqrt{2}}\sin\left(n\frac{2\pi}{T}t + \alpha_n + \frac{\pi}{4}\right)$$

In this case it may be assumed that q_v can be neglected.

By means of the hourly values of sea-surface temperature as given by Defant the curve marked q_τ in Figure 32A has been computed, but it should be observed that the amplitude of the curve is subject to some uncertainty because it depends upon the accuracy of the value of η. Taking into account the location of the stations, the dates on which they were occupied, and the average hourly values of cloudiness, as stated in the tables of meteorological observations (Kuhlbrodt and Reger, 1938), the curve q_r has been computed by means of

Mosby's formula and the Ångström values of back radiation. The difference between these two curves, q_a, represents the amounts of heat given off in unit time to the atmosphere by convection or lost by evaporation. It may again be assumed that the heat used for evaporation is considerably greater than that given off by convection, and that the curve q_a, therefore, roughly represents the diurnal variation of the evaporation.

In the tropics the diurnal variation of evaporation appears to be somewhat similar in character to the annual variation in middle latitudes in the eastern North Atlantic. The maximum evaporation takes place during the early hours of the night, falls off during the latter part of the night towards a secondary minimum in the early morning, rises sharply when the sun appears above the horizon, but drops again to a low minimum in the early afternoon hours. Thus, a semi-diurnal period appears more pronounced than a diurnal, but it is possible that, owing to uncertainties as to the amplitudes of q_r and q_τ, the afternoon minimum, as indicated by the dashed part of the curve q_a, appears too low in this special case. The total evaporation in one day is about 0.5 cm.

It is possible to point out certain observations which substantiate the conclusion that in the tropics a semi-diurnal period prevails. In general, q_r can be expressed as the sum of a constant term and a series of harmonic terms,

$$q_r = \bar{q}_r + \Sigma b_n \sin\left(n\frac{2\pi}{T}t + \beta_n\right)$$

and, similarly, q_τ, can be expressed as a series of harmonic terms,

$$q_\tau = \Sigma a_n \sin\left(n\frac{2\pi}{T}t + \alpha_n + \frac{\pi}{4}\right)$$

Therefore,

$$q_a = \bar{q}_r + \Sigma c_n \sin\left(n\frac{2\pi}{T}t + \gamma_n\right)$$

where

$$c_n = \sqrt{a_n^2 + b_n^2 - 2a_n b_n \cos\left(\beta_n - \alpha_n - \frac{\pi}{4}\right)},$$

$$tg\gamma_n = \frac{a_n \sin\left(\alpha_n + \frac{\pi}{4}\right) - b_n \sin\beta_n}{a_n \cos\left(\alpha_n + \frac{\pi}{4}\right) - b_n \cos\beta_n}$$

We are here interested in the variation of the evaporation and can therefore disregard the constant term. It is evident that each one of the harmonic terms will attain its minimum value if $\alpha_n = \beta_n - \pi/4$. The surplus radiation q_r is, in general, symmetrical around noon and the phase angles of the first two harmonic terms have the values $\beta_1 = 270°$ and $\beta_2 = 90°$. In the tropics, the amplitude of the second harmonic term is relatively great, but in middle latitudes it nearly disappears. It is striking that harmonic analysis of a large number of observations of sea-surface temperatures in the tropics leads to the result that $\alpha_1 = 270° - 45° = 225°$. Hann's analysis of the "Challenger" data gives 227.5, whereas Krümmel and Wegemann from other data obtain 223.8 and 225.8, respectively (Defant, 1932). This indicates that the diurnal variation of the evaporation is as small as possible. There exists, on the other hand, no agreement between the second terms. From the four days dealt with above, Defant's analysis gives $\alpha_2 = 19°$, and the studies by Krümmel and Wegemann give $\alpha_2 = 26°$ and 26.9°, respectively, instead of 45°. Therefore, it may be expected that the semi-diurnal term will be relatively larger. If we make the assumption that the amplitudes b_2 and a_2 are equal, we find that the phase angle of the semi-diurnal evaporation term is about 170°, meaning that the first minimum comes at 3.3^h and the second minimum at 15.3^h. In middle latitudes the diurnal terms dominate both in q_r and q_τ (Wegemann, 1920), and it appears therefore probable that the diurnal variation of the evaporation is more prominent there, and is mainly dependent upon the difference $a_1 - b_1$, because α_1 is close to 225°.

FACTORS WHICH INFLUENCE THE DIURNAL VARIATION OF EVAPORATION

The evaporation from a water surface must, on the one hand, be nearly proportional to the difference between the surplus radiation and the heat used for temperature change of the water, and on the other hand must equal the amount of water vapor which is transported upwards from the surface by processes of eddy diffusion. This upwards transport depends mainly upon the wind velocity, the difference between vapor pressure at the surface and in the air at a short distance from the surface, and the state of turbulence of the air (Sverdrup, 1937). Over the oceans the diurnal variations of the two former factors are relatively small, and it may therefore be assumed that the state of turbulence of the air is of dominant importance. It appears reasonable to assume that shortly after sunrise the turbulence will increase, for which reason the evaporation will also increase. In the tropics

the increase will not continue unimpeded, however, because towards noon the air temperature may become higher than that of the temperature of the sea surface, the stratification becomes stable and the turbulence will be reduced in the early hours of the afternoon. In the late afternoon when the air temperature has dropped below that of the surface, the turbulence will again increase and will reach a maximum some time after sunset. Such a diurnal variation of the turbulence would account for the double period of the evaporation in the central part of the tropics, but in the trade-wind areas and in middle latitudes the air temperature remains below that of the water, and in these circumstances turbulence does not decrease at noon. There, a single period of the evaporation should be expected, probably with minimum in the early forenoon when the temperature difference, water minus air, is smallest (Kuhlbrodt and Reger, 1938). It may be pointed out that over land the evaporation in low latitudes appears to have a single diurnal period with its minimum value at sunrise and its maximum value in the early afternoon. Such a period is in agreement with the fact that over land the surface is warmer than the air throughout the day, and the turbulence has its maximum in the early afternoon hours.

THE DIURNAL VARIATION OF EVAPORATION AND OF THE SPECIFIC HUMIDITY OF THE AIR IN THE TROPICS

In Figure 32B are shown the computed diurnal variations of the heat given off to the atmosphere, q_a, at the four "Meteor" stations, and curves representing the hourly deviations of the specific humidity from the average value, ΔF, and the difference between water and air temperature, $\tau_w - \tau_a$. The minimum of evaporation in the early afternoon hours appears, as was pointed out, to be associated with the fact that in these hours the water was colder than the air, for which reason the turbulence and, consequently, the upwards transport of water vapor was reduced.

The variation of the specific humidity of the air, ΔF, indicates, on the other hand, the presence of a semi-diurnal period which is slightly displaced in relation to the evaporation. These curves are all based on observations from the four days only, but in his discussion of the meteorological observations from the "Meteor," Reger points out that in the tropics the specific humidity shows a pronounced semi-diurnal variation with minima about 4^h and 15^h, and maxima at 10^h and 21^h. Reger's general curve for the tropics is also entered in the figure, and is marked ΔF_T.

If the results as to the evaporation which have been obtained by our example can be generalized it appears that there is a close correspondence between the diurnal variation of the evaporation and that of the specific humidity of the air, as may be expected from a consideration of the processes involved. Variations of the specific humidity in a cube of air at a short distance from the sea surface depend upon the difference between the supply of water vapor through the lower horizontal surface of the cube and the upwards transport of water vapor through the upper horizontal surface. Near the sea surface differences in transport through the vertical surfaces of the cube can be neglected, and if the upwards transport of water vapor associated with the turbulence of the air were constant, the specific humidity would not vary. If now the evaporation increases but the upwards transport remains unaltered the specific humidity must increase. Suppose next that the increase of the evaporation stops so that the supply of water vapor reaches a new but higher value than previously. Then the specific humidity will a little later become constant but will have attained a somewhat higher value. When the evaporation decreases similar considerations are applicable and one is therefore led to the conclusion that under these conditions the specific humidity must vary as the evaporation, but the minima and maxima of the specific humidity must come some time after the corresponding extreme of evaporation. Similarly, a decrease in the upwards transport must lead to an increase of the specific humidity if the evaporation remains constant. Present knowledge of variations of the evaporation and the state of turbulence is too scanty to permit a further examination of the question, but in the tropics the agreement between the variations of the evaporation and the specific humidity is so striking that it appears worth while pointing out. In the trade-wind area a single diurnal period of the specific humidity dominates and there the semi-diurnal period in the evaporation should be expected to be small.

SUMMARY

The annual variation of evaporation is examined by means of the energy equation in an area off the Bay of Biscay and in a part of the Kurosio off southern Japan. In both areas maximum evaporation appears to take place in late fall or early winter, the evaporation in the Kurosio area being nearly three times that off the Bay of Biscay. In both areas the evaporation ceases in summer, but off the Bay of Biscay a secondary maximum occurs in March.

The diurnal variation of evaporation in the tropics is examined in a similar manner. A semi-diurnal period is found which is explained as a result of the varying state of turbulence and which appears to throw light on the previously established semi-diurnal variation of the specific humidity of the air.

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OBSERVATIONS ON THE ALKALINITY[1] OF ESTUARINE WATERS OF THE CHESAPEAKE BAY NEAR SOLOMONS ISLAND, MARYLAND*

By

HARRY F. BRUST AND CURTIS L. NEWCOMBE

Chesapeake Biological Laboratory
and University of Maryland
College Park, Md.

INTRODUCTION

Kolthoff (1926) without particular reference to sea water has defined buffer capacity (alkalinity, in the case of added strong base) of a solution quantitatively as the number of equivalents of added strong base or strong acid required to change the pH of one liter of solution one unit. Buch, in 1930, redefined this concept with reference to sea water as the number of moles of carbonic acid which must be added to one liter of the water in order to change its pH by one unit.

In the subsequent work of Thompson and Bonnar (1931) buffer capacity (alkalinity) is defined as the number of millimoles of hydrogen ions which a unit volume of sea water will neutralize when an excess of standard acid is added. This definition involves no assumptions with respect to the kind or concentration of buffers that may be present. In this procedure, an excess amount of hydrochloric acid is added to a known volume of sea water reducing the pH to about 3.80. Then, by the use of a formula, the number of millimoles of hydrogen ions per liter of sea water is obtained. This takes into consideration the alkalinity of all buffer salts. No allowance was made at that time for the amount of acid necessary to reduce the pH of that amount of sea water if free from buffers. Mitchell and Rakestraw (1933) have discussed this point. They consider the buffer capacity as determined by the equation of Thompson and Bonnar (1931) as apparent buffer capacity. They use neutral sea water free

[1] The committee on Chemical Nomenclature and Procedures of the International Association of Physical Oceanography have recommended that the term "Alkalinity" be used, designating "buffer capacity of sea water," "titratable base," "excess base," etc.

* Contribution No. 38, from The Chesapeake Biological Laboratory.

from carbonates and then reduce the pH to 3.80. The amount of acid required is subtracted from the apparent buffer capacity to give their buffer capacity. This obviously represents the buffering action of carbonates alone and leaves out of consideration other buffering salts including silicates, phosphates and borates which occur only in relatively small quantities.

In this study, the method of Thompson and Bonnar (1931) has been employed with the single exception that a glass electrode[2] was substituted for the colorimetric method of determining pH. No correction has been made for the amount of acid that would be necessary to reduce the pH of the sea water if free of buffers. Thompson and Bonnar, in considering the nature of the buffers in sea water, have clearly pointed out the principal importance of carbonates and the relatively minor role played by silicates, phosphates and borates. Mitchell and Rakestraw (1933) in making the aforementioned correction considered the buffer action as due to carbonates alone, while pointing out the relatively insignificant role played by additional buffer salts present.

Studies in progress at this laboratory are designed to prepare a comprehensive table along the lines of that of Mitchell and Rakestraw working in Narragansett Bay, which will provide corrections for the effects of salts upon the hydrogen ion activity and for the amount of acid necessary to reduce the carbonate free sea water to a pH of approximately 3.8. The preparation of this table will extend the use of the glass electrode for determining alkalinity.

EXPERIMENTAL

Apparatus. In order to determine the pH of the sea water, after the addition of a known amount of standard hydrochloric acid from a burette, a Beckman pH meter equipped with a glass electrode was employed. A small electric motor provided with an efficient stirrer was used to insure thorough mixing of the solution.

Method. A known volume of 0.009745 N hydrochloric acid was added rapidly to 100 ml. of sea water until the pH was about 3.80. By using the motor driven stirrer it was found that the solution came rapidly to equilibrium after the acid had been added and did not change. The alkalinity, as described above, was determined immedi-

[2] Professor T. G. Thompson, Oceanographic Laboratory, University of Washington, has informed us, in a personal communication dated Feb. 5, 1940, that the satisfactory use of the glass electrode for this purpose has been demonstrated in his laboratory.

ately on board the boat. The chlorinity of each sample was determined by a standard procedure (Mohr's Method), and the chlorinity as found in parts per thousand was corrected to express as grams per liter at 20° C. Knowing the volume of hydrochloric acid used and the resulting pH, the alkalinity was calculated using the formula of Thompson and Bonnar (1931).

Figure 33. Location of principal sampling stations (numbered points) in the Patuxent River (2 = 102).

Standard Used. *Hydrochloric acid:* Two liters of about 0.1 N hydrochloric acid was made up in a pyrex flask and standardized against pure sodium carbonate. The acid was found to be 0.09745 N. From this stock solution a volumetric dilution was made with distilled water producing a 0.009745 N hydrochloric acid solution which was used in the work. The dilution was made in order to minimize titration errors in the standardization.

Sodium carbonate: Baker's C. P. sodium bicarbonate was recrystallized twice and dried. This purified bicarbonate was heated to constant weight at 280° C. The resulting pure sodium carbonate was cooled in a desiccator over calcium chloride and stored in a glass-stoppered bottle.

Standard pH *solution:* This standard buffered solution of known pH(± .02 pH unit) was constantly used to check the Beckman pH meter.

Accuracy of Results. The volumetric measurements and gravimetric weighings were all made with an accuracy of two parts per thousand or less. The pipettes used were corrected for temperature variations in the sea water. The samples were collected in clean pyrex flasks, and the alkalinity determined within fifteen minutes of sampling. Silicates from soda glass can measurably raise the alkalinity if allowed to stand for any length of time, Mitchell and Rakestraw (1933). The Beckman pH meter had a temperature control which was adjusted for changes in temperature of the sea water. The accuracy of the meter was within ± 0.02 pH unit. Duplicate runs made on the same sample demonstrated that the amounts of acid used to produce a final pH of 3.80 were in each case within 0.02 ml. of each other.

Results

Determinations have been made in waters of widely different chlorinities in the Bay proper—Stations 110 to 102 and in the lower reaches of the Patuxent River—Stations 5 to 18 (Figure 33). These waters show marked differences with respect to chlorinity, turbidity and nutrient salts (Newcombe, Horne and Shepherd, 1939: Newcombe and Lang, 1939). The conspicuous variations in turbidity following heavy rains and the seasonal differences in the amounts of suspended particles are reflected in the chemical equilibria that appear to exist. The alkalinity-chlorinity factor, called the specific buffer capacity by Mitchell and Rakestraw (1933), has not been found to be a constant one over the range of chlorinities studied. Table I is constructed on a basis of decreasing chlorinity 11.85 grams per liter to 4.39 grams per liter. Figure 34 shows more clearly the increase in the alkalinity-chlorinity factor with decrease in the chlorinity of estuarine waters. Thompson and Bonnar (1931), working with estuarine waters off the north Pacific coast, demonstrated this relationship. It was also shown to be true by Mitchell and Solinger (1934) of the estuarine waters of Narragansett Bay.

TABLE I

ALKALINITY AND ALKALINITY—CHLORINITY FACTOR OF PATUXENT RIVER AND CHESAPEAKE BAY WATERS. STATIONS AND DEPTHS ARRANGED ACCORDING TO DECREASING CHLORINITIES. SEPTEMBER 8, 1939

Stations	*Depth in Meters*	*Chlorinity grams per liter at 20° C.*	*Alkalinity*	$\frac{Alk.}{Cl}$
110	15	11.85	1.674	0.1413
12	17	9.14	1.416	0.1549
110	7.5	8.52	1.322	0.1552
8	35	8.51	1.411	0.1658
102	15	8.49	1.367	0.1610
102	7.5	8.48	1.385	0.1633
102	1	8.46	1.367	0.1616
110	1	8.43	1.329	0.1577
12	8.5	8.12	1.373	0.1691
8	17.5	7.70	1.348	0.1751
8	1	7.46	1.329	0.1781
12	1	6.80	1.254	0.1844
16	7	5.98	1.134	0.1896
18	6	5.61	1.082	0.1929
16	1	5.25	1.042	0.1985
18	1	4.39	0.942	0.2147

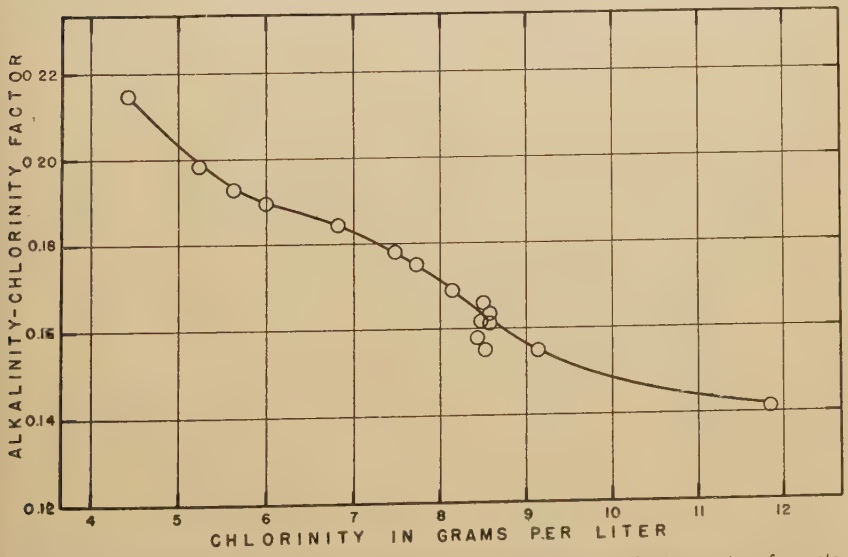

Figure 34. Alkalinity-Chlorinity Factor of surface, intermediate and bottom waters from stations in the Patuxent River and Chesapeake Bay. Time—September 8, 1939.

DISCUSSION

Mitchell and Rakestraw (1933) found the alkalinity-chlorinity factor of Atlantic water off Cape Cod to be about 0.119. The estuarine waters of Narragansett Bay gave a ratio of 0.175 at a chlorinity of 4.5 grams per liter, 0.154 at a chlorinity of 7 grams per liter and 0.137 at 11 grams per liter. Corresponding ratios for Chesapeake estuarine waters have been found to be 0.212, 0.183, and 0.143. These values, it is noted, are somewhat higher than those referred to above. As previously mentioned, our values are uncorrected. The corrected ratios probably would closely approximate those for the northern waters. That a pronounced difference has been shown to exist in the apparent buffer capacity between the typical Bay waters and the less saline river waters seems significant. Furthermore, the apparently close agreement with the results of Mitchell and Solinger (1934) is not necessarily to be expected. The modifying conditions of soil, land drainage, photosynthetic action, and pollution are obviously quite different in the Chesapeake Bay area from those in Narragansett Bay and might reasonably be expected to show significant differences in respect to buffering properties. Such differences have been found to exist between Bay waters having fairly similar chlorinities but of different origins.

The manuscript has been given critical reading by Professor Martin Kilpatrick of the University of Pennsylvania, to whom the writers wish to express sincere thanks.

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CONTRIBUTION TO THE QUESTION OF THE EQUATORIAL COUNTER CURRENT

By

R. B. MONTGOMERY
National Research Council, Washington

AND

E. PALMÉN
Thalassological Institute, Helsingfors

1. EXAMINATION OF THE THEORY FOR THE EQUATORIAL CURRENTS

The question of the dynamics of the equatorial counter currents of the several oceans was scarcely brought nearer solution by the research of recent years. The attempt of Sverdrup (1932), which Defant (1935) has further pursued, to explain the counter current as a result of the asymmetry about the equator of the westward-flowing north and south equatorial currents, does not suffice. This may be shown by the following short exposition.

With symmetric wind distribution about the equator (doldrums coinciding with equator) the dynamic balance can be illustrated schematically by the shape of the sea surface and of the internal density discontinuity in Figure 35A. If the doldrums lie north of the equator, as is the normal case in both the Atlantic and Pacific Oceans, the condition of dynamic balance still merely stipulates that along a meridional section the sea surface and the internal boundary must have a slope giving equilibrium with the Coriolis force on the longitudinal motion. With a westward current corresponding at every vertical of the meridional section to the strength of the trade winds one would expect the calm zone to be characterized by stagnant water (or, taking lateral friction into account, by a weak westward current). For this case dynamic balance requires a condition as in Figure 35B. The equator is distinguished by a trough in the sea surface and a ridge in the internal boundary; the doldrums, however, are revealed merely by a horizontal course of these two surfaces. On the other hand, the presence of a counter current demands a scheme of the type in Figure 35C, which will be recognized from the papers of Sverdrup and Defant.

It is therefore not allowable to consider the counter current as a part of the equatorial flow necessary for a balance of forces in the meridional direction. The circumstance that the mass distribution actually corresponds to the schematic representation of Figure 35C merely signifies that this distribution is dynamically required in the presence of a counter current asymmetric to the equator. The cause of the counter current must be sought elsewhere.

One is thus brought back to the thoughts expressed by Ekman as early as 1906, for these appear to offer a foundation for the present investigation.

When a uniform and constant wind covers the whole surface of a homogeneous limited ocean of uniform depth the integral from top to bottom of the water transport must everywhere be zero, because

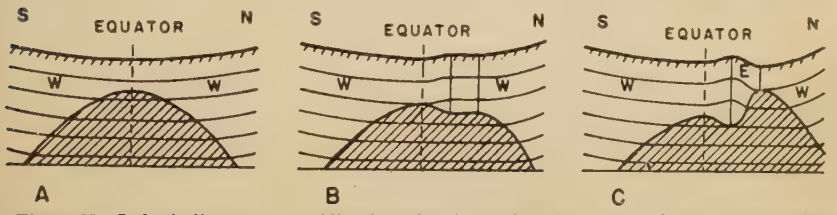

Figure 35. Isobaric lines on a meridional section (extending to a depth of about two hundred meters) of the tropical waters in an idealized two-layered ocean. The lower layer is motionless and the waters in the upper layer flow westward ("W") or eastward ("E") as indicated. A, symmetry about the equator and no counter current. B, a stagnant zone north of the equator. C, a counter current north of the equator.

there are no preferred regions for it to become finite. The transport of the pure *drift current* is perpendicular *cum sole* to the wind direction. According to Ekman (1906, p. 532) the rise of the sea surface nearly coincides with the wind direction. There is a *deep current* uniform from top to bottom directed perpendicular *contra solem* to the rise of the sea surface. Its speed is always less than that of the drift current at the surface, and is approximately proportional to the ratio of the depth of frictional influence to the depth of the ocean. When this ratio is a small fraction, the *bottom current* becomes negligible so that there is balance between the wind stress and the pressure gradient associated with the slope of the sea surface. This means that there is balance between the transport of the drift current and the transport of the deep current.

Ekman regards the equatorial currents as a modification of this very simple scheme. The northeast and southeast trade winds blow over two zones of the ocean; between them and on the poleward sides are calm zones. It is assumed, following the preceding result, that

the component of the pressure gradient in the direction of the wind (longitudinal) is uniform throughout the ocean, and of such magnitude that its integral over the volume of the ocean balances the integral of the wind stress over the surface of the ocean. Locally there is not balance between these two forces, but bottom friction balances the pressure gradient in the calm zones and balances the difference between wind stress and pressure gradient in the trade wind zones. To produce this bottom friction the deep current must have longitudinal components of the same order of magnitude as the surface velocity of the pure drift current.

Associated with the deep current are meridional pressure gradients and deformations of the sea surface. In the trade wind zones the deep current flows westward as the *equatorial currents*, in the zone of doldrums it flows eastward as the *equatorial counter current*. Thus according to Ekman the counter current is a compensation current which flows downslope as a consequence of the longitudinal pressure gradient maintained by the trades.

Actually the ocean is vertically stable. There is a surface layer, which may be considered vertically homogeneous, below it a layer of strong stability (*Sprungschicht*), and then a more gradual increase downwards of potential density. Due to this stability there is no necessity for the longitudinal pressure gradient to extend downward to great depth. As will be discussed in Section 3, one may expect that this gradient will not extend deeper than the bottom of the *Sprungschicht*. It should be nearly constant from the sea surface to the bottom of the surface layer, and then decrease to zero at the bottom of the *Sprungschicht*. In the simplified numerical estimates which will follow, the gradient will be assumed constant from sea surface to middle of *Sprungschicht*, and to vanish below the latter depth. Hence the gradient must be much more intense than in a homogeneous ocean.

A longitudinal pressure gradient of similar type has already been observed in the Caribbean Sea by Parr (1937), who found a slope of the sea surface rising westerly along the axis of the Carribbean Current, amounting to $17 \cdot 10^{-8}$ (about 30 cm in 1750 km). This estimate was reduced to $13 \cdot 10^{-8}$ by Sverdrup (1938, p. 287), who further found the vertical integral of the pressure gradient to be 3.6 dyne cm^{-2}. The trade winds in the Caribbean in March and April, when the mass distribution used in these calculations was obtained, blow about 9 m sec^{-1}, which Sverdrup showed to exert a nearly compensating stress on the sea surface.

The longitudinal slope of the sea surface in the equatorial Atlantic

Ocean may be estimated from the wind strength as follows. The quadratic relationship

$$\tau_o = \varrho \gamma^2 W^2 \tag{1}$$

gives the wind stress τ_o in terms of the wind speed W, if the coefficient γ^2 is known. In this formula ϱ represents air density. According to the different estimates, especially those of Taylor (1916), Ekman (1928), Rossby and Montgomery (1935, pp. 12–14), Sverdrup (1936, pp. 12–15) and Palmén and Laurila (1938, pp. 29–31), a probable value of γ^2 is about $25 \cdot 10^{-4}$. Thus one obtains, using the mean values of wind speed in Table I, a wind stress of 0.72 dyne cm^{-2} for

TABLE I

MEAN MONTHLY WIND VELOCITY FROM SHIP OBSERVATIONS IN THE ATLANTIC TRADE WIND ZONES, IN M SEC^{-1} (FROM SHAW, 1936, P. 277)

Month	*N.E. trades**	*S.E. trades†*
I	5.3	5.9
II	5.8	6.3
III	5.6	6.0
IV	6.0	6.7
V	5.5	6.4
VI	5.0	6.7
VII	4.6	5.8
VIII	3.7	6.7
IX	4.3	6.4
X	3.3	6.1
XI	4.4	6.7
XII	5.2	6.4
Mean	4.9	6.3

* 10°–30° N. between 30° W. and the African coast.
† 10°–20° S., 0°–10° E. and 0°–20° S., 0°–10° W.

the northeast trades and 1.19 dyne cm^{-2} for the southeast trades. In view of the quadratic relation one should properly use somewhat greater values since the wind is not constant.

The average westward component of the wind stress over the trade wind zones 10°–30° N. and 0°–20° S. may then be about 0.75 dyne cm^{-2} and over the whole zone between 30° N. and 20° S. about 0.6 dyne cm^{-2}. This stress must be balanced by the eastward pressure gradient of the whole zone.[1] If the *Sprungschicht* is 100 meters

[1] Actually the regions north and south of the trade winds should be taken into consideration. Thus the Gulf Stream System could be regarded as a return

below the surface, the pressure gradient must be about $6 \cdot 10^{-5}$ cm^{-2} g sec^{-2}. The corresponding slope of the sea surface is $6 \cdot 10^{-8}$, or 24 cm in 4000 km. Over this distance the counter current would attain a speed of $\sqrt{2gh} = 217$ cm sec^{-1} if there were no retarding friction. The actual speed of the counter current is only about 50 cm sec^{-1}, this speed being attained at a point nearer the origin than the downstream end of the current. Downstream from this point, therefore, the pressure gradient must be approximately balanced by a retarding force—whether this is vertical friction or lateral friction is difficult to determine definitely.

Ekman's (1906, pp. 578–579) discussion of wind-produced currents in a stratified ocean may be applied to the counter current. Lateral friction is neglected, and it is assumed that the current is very long so that acceleration is negligible and that the net meridional transport in each layer of constant potential density is zero. There must be a stress of about 0.6 dyne cm^{-2} transmitted in some manner to the ocean bottom from the *Sprungschicht*. In particular, if the water below the *Sprungschicht* is continuously stratified, the direction of flow must be due eastward at all depths below the *Sprungschicht*. The retarding force on the water above the *Sprungschicht* must then be transmitted directly as a shearing stress all the way from the bottom. For a depth of 4000 meters and an eddy viscosity of, for instance, 10 cm^{-1}g sec^{-1}, the magnitude of the surface current would have to be 24,000 cm sec^{-1}. The actual current is of a much smaller order of magnitude, so this treatment obviously has no application.

But suppose the stratification is discontinuous, so that there are a number of homogeneous layers below the *Sprungschicht*. Then it is permissible to have meridional components of velocity, provided there is no net meridional transport for each layer. If the thickness of each layer exceeds twice the depth of frictional influence, there is a longitudinal gradient current of v_1 in the bottom layer, $3v_1$ in the next layer, $5v_1$ in the next, and so on (Ekman, 1906, p. 579). In this case v_1 would have to be of the order of magnitude of 15 cm sec^{-1}. Even if there were only two layers, the necessary velocity immediately below the *Sprungschicht* would thus have to be about 45 cm sec^{-1}. In the axis of the Atlantic counter current at the sea surface the speed certainly does not exceed 80 cm sec^{-1} (Koninklijk Nederlandsch Meteorologisch Instituut, 1926, charts of "Equatorialstroo-

flow similar to the equatorial counter current. North and south of the trades, however, the prevailing westerlies are present to drive the return flow, so it seems permissible as a first approximation to assume balance of longitudinal forces within the zone 30° N. to 20° S.

men"; Schott, 1935, Tafel XXIX and Tafel XXX; Schott, 1939, Tafel 26 and Tafel 27; in the last paper only the eastern half of the charts is applicable), and the decrease from the surface to below the *Sprungschicht* is about 50 cm sec^{-1} (Montgomery, 1938, Fig. 7). So the speed immediately below the *Sprungschicht* does not exceed 30 cm sec^{-1}, which is probably insufficient for the existence of even two layers of the type discussed. Furthermore, the vertical distribution of density in the deep water indicates that probably there would have to be more than just two layers in order for each to be sufficiently homogeneous.

It must be concluded that the retarding force on the counter current is not transmitted to the ocean bottom. Nevertheless it is possible that the retarding force is vertical friction on the bottom of the counter current, for this vertical friction may act only to accelerate the underlying water. If a shearing stress τ is absorbed by an underlying layer of thickness D, after moving a distance x downstream along the counter current the layer would attain a speed of $\sqrt{2\tau x/D\varrho}$. After moving a distance of 3000 km a layer 1000 meters thick subject to 0.6 dyne cm^{-2} would therefore have a speed of 60 cm sec^{-1}. Such a speed certainly does not occur. But the layer in question may have sufficient meridional motion so that a given water mass does not remain long enough under the counter current to be greatly accelerated. It is a fact that the motion at depths of 150–400 meters under the eastern half of the Atlantic Equatorial Counter Current has a pronounced northward component (Montgomery, 1938, pp. 50–51).

The vertical shear at the *Sprungschicht* in the counter current is about $6 \cdot 10^{-3}$ sec^{-1} (Montgomery, 1939). To transmit the necessary stress of 0.6 dyne cm^{-2} the eddy viscosity must have a value of 100 $cm^{-1}g\ sec^{-1}$. Montgomery found that the vertical eddy diffusivity in the same place does not exceed 0.4 $cm^{-1}g\ sec^{-1}$, and concluded that its value is probably only a tenth of this. So the former coefficient would have to be 250 to 2500 times as great as the latter. Taylor (1931a, 1931b) gives the corresponding ratio as only 5 to 50 for cases where the stability ranges between $0.075 \cdot 10^{-5}$ and $1.5 \cdot 10^{-5}$ cm^{-1}, whereas in the present case the stability is about $5 \cdot 10^{-5} cm^{-1}$ (Montgomery, 1939). This comparison makes it seem doubtful that the vertical eddy viscosity can be as great as 100 $cm^{-1}g\ sec^{-1}$, and hence that the retarding force on the counter current is essentially vertical rather than lateral friction.

Rossby (1936, p. 5–6) has drawn attention to the fact that the winds (in all seasons of the year) exert an anticyclonic torque on the waters of the North Atlantic (as well as of the South Atlantic) and

that, since bottom friction is apparently far too slight to exert the necessary counteracting torque, lateral friction provides the dominant cyclonic torque. It seems likely, therefore, that also in the equatorial counter current the dominant retarding force is lateral friction.

In the following section the presence of a longitudinal pressure gradient along the equator will be demonstrated, and its magnitude will be found to agree with the prediction of Ekman's theory. It is thus proven that the counter current is produced by this gradient maintained by the trade winds. But, whereas Ekman ascribes the retarding force to vertical friction, it appears at present more likely that this should be ascribed to lateral friction, at least to large extent.

The idea that the trade winds maintain a westward rise of sea level was advanced by a number of authors during the nineteenth century. It apparently originated with Franklin (1786, p. 315), who wrote that the Gulf Stream "is probably generated by the great accumulation of water on the eastern coast of America between the tropics, by the trade winds which constantly blow there." The first to explain the Atlantic Equatorial Counter Current (Guinea Current) in this way seems to have been A. G. Findlay. Pillsbury (1890, p. 472) quotes him as saying that "later investigation seems to point to the fact that it is a flowing back of the waters heaped up to the westward by the prevalent winds."

2. THE OBSERVED LONGITUDINAL PRESSURE GRADIENT

The trades are not purely east winds, as assumed in the discussion above, so it is not a simple matter to evaluate the "longitudinal" or axial pressure gradient in the water. Under the northeast trades there is a "northward" transport of surface water due to the pure drift current, and a "southward" transport associated with the axial gradient. The vertical integral of the velocity gives a net current which flows predominantly westward and is known as the equatorial current. Associated with it is a "meridional" or cross-stream gradient. The axial gradient is, specifically, the one directed along the path of the net (north or south) equatorial current. The path must be known accurately in order to avoid including part of the cross-stream gradient. But, since the actual current direction varies with depth, it is not easy to locate this path.

Professor Albert Defant has kindly placed at our disposal his chart of the absolute topography (corresponding to a standard atmospheric pressure) of the surface of the Atlantic Ocean, as yet unpublished. This shows firstly that the available observations are still insufficient to obtain a clear picture of the average topography, for there are many

irregularities which are undoubtedly of transient nature.[2] Secondly, it is found that the chart definitely demonstrates the presence of a longitudinal pressure gradient, for between 10° N. and 30° N. and between 5° S. and 25° S. the contours run predominantly north-south. At 18° N. the surface is indicated as more than 45 cm higher on the American side than on the African, at 15° S. the difference is about 30 cm. The former value, representing an average slope of $9 \cdot 10^{-8}$, is large because it includes not only the axial gradient along the Atlantic North Equatorial Current but also a large part of the cross-stream gradient, the current having a pronounced southward component in the eastern half of the ocean. This is schematically described in Figure 36. It does not seem practicable to separate the

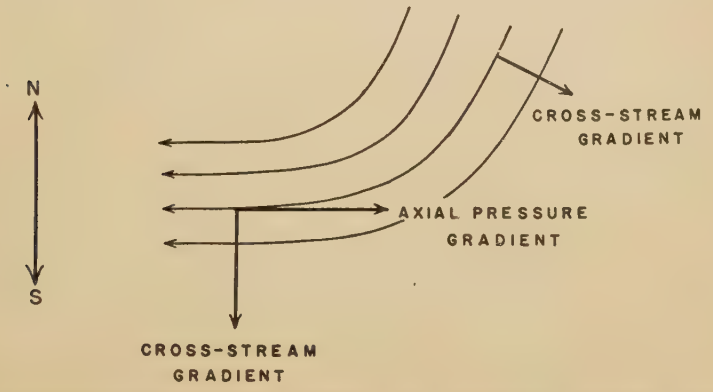

Figure 36. Scheme of the cross-stream gradient in the Atlantic North Equatorial Current.

axial and cross-stream components in this current. Professor Defant's charts for deeper surfaces show that cross-stream pressure components predominate at 100 db and 200 db, and that all gradients in tropical regions become very small indeed at 500 db.

In this connection the slope of the sea surface in the region of the Atlantic North Equatorial Current as revealed by Professor Defant's chart may be somewhat more closely examined. The course of the contours of the sea surface for about 20° N. is schematically copied in Figure 37A, and the contours of the 100 db surface in Figure 37B. The slope of the sea surface corresponds to the combined influence

[2] It would be an interesting problem to find out the extent to which these irregularities are to be ascribed to the weather conditions at the time of the observations. In any case one may well assume that considerable variations in the depth of the *Sprungschicht* arise from this cause.

of the axial pressure gradient, which coincides approximately with the direction of the northeast trades, and of the cross-stream gradient associated with the axial flow. Since the equatorial current at the surface may be regarded as the resultant of a pure drift current and

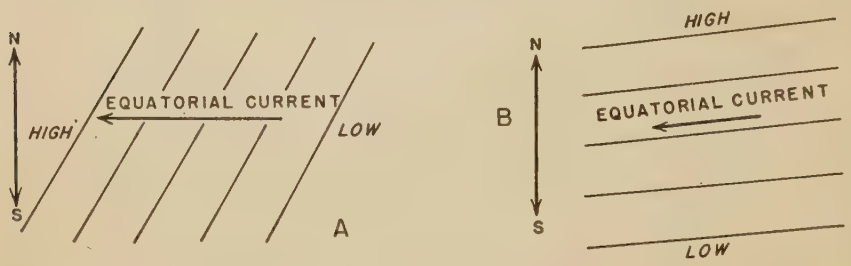

Figure 37. Schematic representation of the topography of two isobaric surfaces in the north equatorial current. A, sea surface. B, 100 db surface.

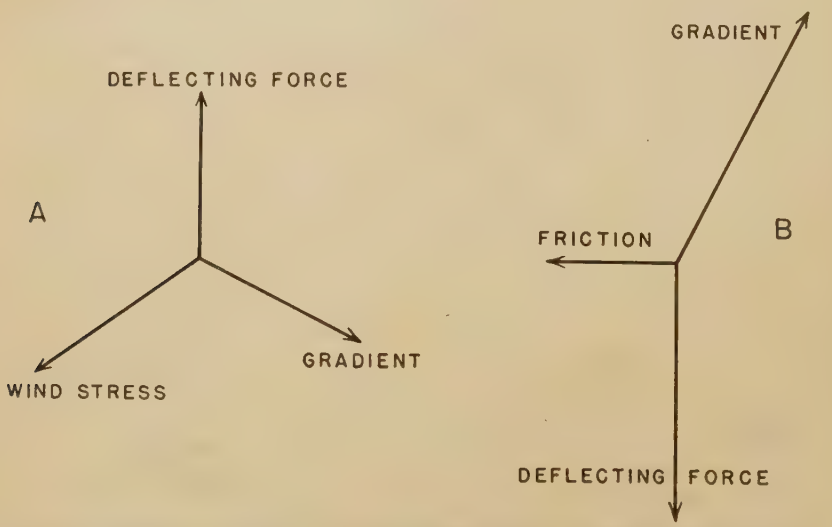

Figure 38. Equilibrium of forces on a vertical column of water extending from the sea surface to the bottom of the current. A, north equatorial current. B, equatorial counter current.

of a gradient current parallel to the contours, the water here flows uphill. At the depth of 100 db., however, the axial component of the gradient is very small because it is almost entirely limited to the surface layer, and the current flows approximately as a pure gradient current along the contours of Figure 37B. The same scheme, modi-

fied for the opposite sense of the Coriolis acceleration, naturally holds for the south equatorial current. Thus for each depth the equatorial current can be constructed from a drift-current spiral and from the gradient current at the depth in question.

The circumstance that the cross-stream gradient in the Atlantic North Equatorial Current decreases upward from the 100 db. surface is associated with the poleward increase of density of the surface layer. It is thus primarily a thermal effect, *i.e.*, an effect of heat and mass exchange across the sea surface.

Since the wind is very weak over the counter current, the direction of motion may be expected to be quite uniform with depth. Furthermore the axis of the Atlantic Equatorial Counter Current is fairly well defined by the salinity and oxygen distribution (Montgomery, 1938, Charts 9–18). Accordingly we have attempted to determine the axial gradient along this current, but the values from different stations are too scattered to give even a rough estimate. This is apparently because the cross-stream gradient is intense (Montgomery, 1938, Figs. 6 and 7).

The balance of forces for a vertical column of water in the north equatorial current and in the counter current is shown schematically in Figures 38A and B respectively. In the first case the wind stress is approximately balanced by the pressure gradient and by the Coriolis force, for friction with the deep water as well as with the water flanking the current on both sides appears to be of lesser magnitude. On the other hand the axial gradient in the counter current can be balanced by no other force than vertical or lateral friction.

The ideal locality for determining the longitudinal gradient is at the equator itself. Here there can be no cross-stream gradient because deflecting force and compensating pressure gradient vanish.

Table II and Figure 39 show the anomaly of dynamic height, of the sea surface and other isobaric surfaces, above the 1000 db surface for stations near the equator in the Atlantic. Assuming the 1000 db surface to be level, the values give the topography of the various surfaces (corresponding to a standard atmospheric pressure). It has been found previously that in the tropics the 1000 db surface seems to be a more suitable reference plane than deeper surfaces (Montgomery, 1938, p. 19). The *Atlantis* data is from *Bulletin Hydrographique pour l'année 1931*, that for *Dana* is from *Dana Report No. 12* (1937), and that for *Meteor* is from Wüst (1938).

It is seen that the resulting values of sea level are consistently higher at the western stations than at the eastern ones. In order to obtain mean values for the slope of the different isobaric surfaces, the

western and eastern stations within one degree of the equator have been averaged separately. The distance between the centers of the two groups is 3700 km. The average heights and resulting slopes are

TABLE II

ANOMALY OF DYNAMIC HEIGHT IN DYNAMIC CENTIMETERS FOR STATIONS NEAR THE EQUATOR IN THE ATLANTIC OCEAN

Ship	*Atlantis*	*Atlantis*	*Meteor*	*Meteor*	*Meteor*	*Meteor*	*Dana*
Station	1180	1179	257	258	211	212	4000
Latitude	0° 20′ N.	0° 45′ N.	0° 58′ S.	0° 36′ N.	1° 01′ S.	0° 36′ N.	0° 31′ S.
Longitude	43° 33′ W.	42° 38′ W.	38° 44′ W.	37° 06′ W.	30° 00′ W.	29° 12′ W.	11° 02′ W.
Date	22 III 32	21 III 32	4 II 27	6 II 27	18 X 26	19 X 26	4 III 30
0 db	140.6	132.0	137.7	138.3	134.7	138.1	124.7
50 db	117.6	109.0	115.2	116.2	113.2	115.6	102.9
100 db	98.9	96.0	94.7	96.5	94.5	98.2	92.1
150 db	89.0	86.0	82.5	85.4	84.9	88.3	84.4
200 db	80.6	78.0	75.2	77.9	77.6	80.8	76.9
300 db	66.3	64.4	62.7	64.8	63.9	67.3	63.2
400 db	53.4	51.4	51.5	52.8	51.7	55.2	52.0
500 db	43.6	41.2	41.5	42.3	41.3	44.3	41.8
600 db	33.3	32.0	32.3	32.9	32.1	34.3	32.4
700 db	25.3	23.4	23.6	24.0	23.2	24.8	23.7
800 db	16.2	15.0	15.3	15.5	14.8	15.8	15.3
900 db	7.9	7.0	7.4	7.6	7.0	7.4	7.4
1000 db	0	0	0	0	0	0	0

Ship	*Meteor*	*Meteor*	*Meteor*	*Meteor*	*Meteor*	*Meteor*
Station	243	225	242	233	232	240
Latitude	1° 18′ S.	0° 03′ N.	0° 40′ S.	0° 16′ N.	1° 08′ N.	0° 31′ N.
Longitude	9° 31′ W.	9° 30′ W.	4° 57′ W.	1° 03′ W.	0° 59′ W.	1° 52′ E.
Date	29 XII 26	17 XI 26	27 XII 26	27 XI 26	26 XI 26	20 XII 26
0 db	119.3	125.1	124.2	123.2	126.1	119.7
50 db	101.6	107.1	103.1	103.4	103.5	101.3
100 db	92.3	96.5	92.4	94.5	94.2	92.8
150 db	84.8	88.4	84.6	86.4	86.1	84.8
200 db	77.4	80.9	77.0	78.5	78.1	77.0
300 db	63.6	66.3	63.1	64.4	63.9	62.8
400 db	52.0	53.8	51.6	52.9	52.5	51.2
500 db	42.1	43.5	41.4	42.7	42.1	41.3
600 db	32.7	34.0	32.0	33.1	32.3	32.0
700 db	23.8	24.9	22.9	23.8	23.2	22.9
800 db	15.5	16.3	14.5	15.1	14.8	14.4
900 db	7.5	8.1	7.0	7.2	7.1	6.9
1000 db	0	0	0	0	0	0

given in Table III. The straight lines in Figure 39 were drawn from the values of this table. It is found that the pressure gradient becomes very small already at 150 meters depth. The vertical integral

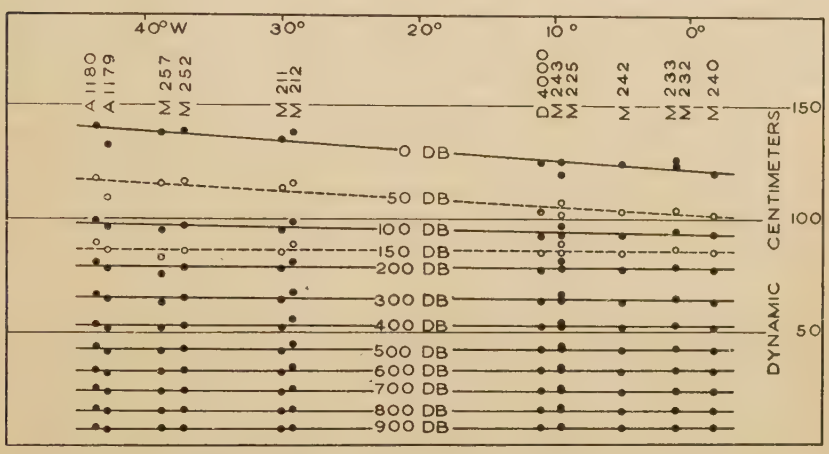

Figure 39. Anomaly of dynamic height of isobaric surfaces along the equator in the Atlantic Ocean. The scale exaggerates the slopes of the isobaric surfaces about $2 \cdot 10^6$ times.

TABLE III

AVERAGE ANOMALY OF DYNAMIC HEIGHT FOR 5 WESTERN STATIONS (*Atlantis* 1180, 1179; *Meteor* 257, 258, 212) AND FOR 5 EASTERN STATIONS (*Dana* 4000; *Meteor* 225, 242, 233, 240) WITHIN ONE DEGREE OF THE EQUATOR IN THE ATLANTIC OCEAN AND RESULTING SLOPE OF ISOBARIC SURFACES

Isobaric surface db	*Western stations dynamic cm.*	*Eastern stations dynamic cm.*	*Slope*
0	137.3	123.4	$3.8 \cdot 10^{-8}$
50	114.7	103.6	3.0
100	96.9	93.7	0.9
150	86.2	85.7	0.1
200	78.5	78.1	0.1
300	65.1	64.0	0.3
400	52.9	52.3	0.2
500	42.6	42.1	0.1
600	33.0	32.7	0.1
700	24.2	23.6	0.2
800	15.6	15.1	0.1
900	7.5	7.3	0.1

of the pressure gradient from sea surface to 150 meters according to these values is 0.29 dyne cm^{-2}.

Suitable published material from the Pacific Ocean is limited to four *Dana* stations (*Dana Report No. 12*, 1937). Table IV gives the station values, as well as the slopes resulting from the difference between the average for the three western stations and the single eastern station, the intervening distance being 14000 km.

TABLE IV

ANOMALY OF DYNAMIC HEIGHT IN DYNAMIC CENTIMETERS FOR *Dana* STATIONS NEAR THE EQUATOR IN THE PACIFIC OCEAN AND RESULTING SLOPE OF ISOBARIC SURFACES

Station	*3775*	*3756*	*3767*	*Mean*	*3558*	
Latitude	0° 02′ S.	0° 46′ S.	1° 28′ S.		0° 18′ S.	
Longitude	131° 18′ E.	134° 12′ E.	138° 43′ E.	134° 44′ E.	99° 07′ W.	*Slope*
Date	29 VII 29	15 VII 29	23 VII 29		18 IX 28	
0 db	192.0	199.0	201.8	197.6	135.0	$4.5 \cdot 10^{-8}$
50 db	161.1	168.4	172.1	167.2	120.8	3.3
100 db	131.2	140.3	138.8	136.8	109.7	1.9
150 db	109.5	117.5	115.6	114.2	100.5	1.0
200 db	95.2	102.2	97.6	98.3	92.0	0.4
300 db	74.1	78.8	73.9	75.6	75.9	0.0
400 db	59.8	61.7	58.1	59.9	61.4	−0.1
500 db	47.2	48.7	46.0	47.3	49.4	−0.2
600 db	36.1	37.4	35.2	36.2	38.2	−0.1
700 db	25.9	27.1	25.1	26.0	27.4	−0.1
800 db	16.6	17.5	16.0	16.7	17.4	0.0
900 db	8.0	8.5	7.8	8.1	8.3	0.0
1000 db	0	0	0	0	0	0

In the Pacific also the sea surface slopes upward from east to west along the equator, at about the same angle as in the Atlantic. The longitudinal pressure gradient extends deeper in the Pacific, for there is still an appreciable gradient at 200 meters. The integral of the gradient from surface to 300 meters is 0.45 dyne cm^{-2}.

Finally Figures 40 and 41 give a schematic representation of the topography of the sea surface in the vicinity of the equator, the first for the doldrums symmetrical with the equator and the second for a northward displacement of the doldrums. The velocity distribution with respect to the axis of the counter current is identical in the two cases. For the symmetrical distribution the counter current is

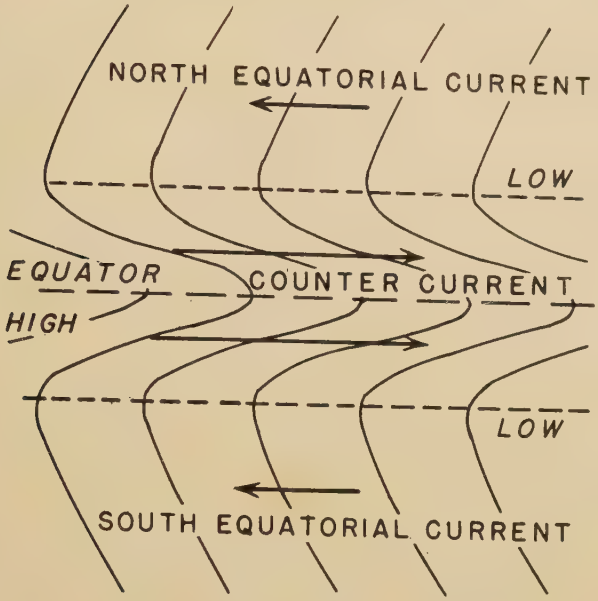

Figure 40. Scheme of the topography of the sea surface with symmetry about the equator.

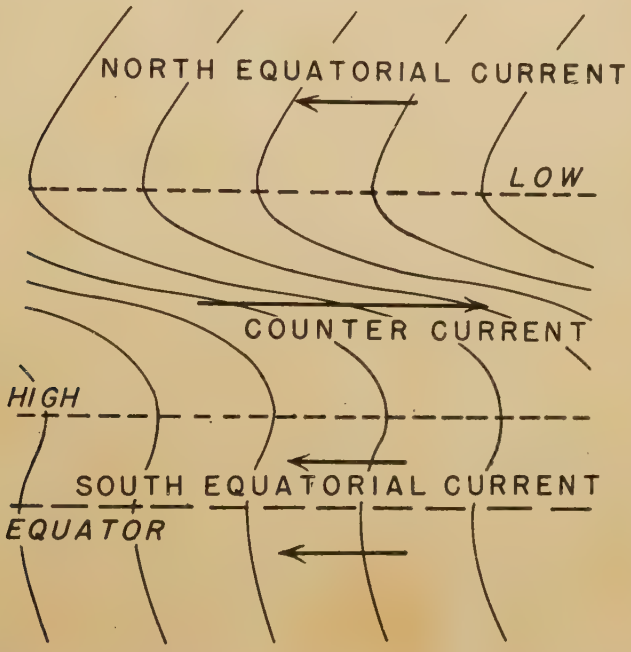

Figure 41. Scheme of the topography of the sea surface with a displacement of the counter current northward from the equator.

bounded by troughs. The balance of forces for the half of the current in the northern hemisphere is as shown in Figure 38. For the asymmetrical distribution in Figure 41 conditions are more complicated. The northern trough lies, as in the previous case, between the north equatorial current and the counter current. The meridional slope of the sea surface in the counter current must however be greater corresponding to the greater magnitude of the Coriolis force. The southern boundary of the counter current coincides with a ridge north of the equator, not with a trough as in the previous case, and along the equator lies a trough instead of a ridge. Figure 41 corresponds to the schematic cross-section in Figure 35C.

Figure 41 is drawn under the assumption that the southeast trades are pure east winds, so that at the equator, where the Coriolis force vanishes and the westward wind stress is balanced by a pressure gradient directed eastward, the contours run north-south. Taking into account the south component of the southeast trades, however, the contours must cut the equator at an acute angle. The contours must run more southwest-northeast and, if accelerative forces can be neglected as well as the component of friction normal to the wind, they must cross the wind at right angles. This circumstance brings about a further asymmetry about the equator, which one can recognize clearly on the charts placed at our disposal by Professor Defant. In this respect the modification by the monsoon of the southeast trades near the African coast has a strong effect.

3. THE DEPTH OF THE LONGITUDINAL PRESSURE GRADIENT

It was assumed in Section 1 that the longitudinal pressure gradient does not extend below the principal *Sprungschicht.* This conclusion was based on the following considerations.

For simplicity consider at first a closed basin of resting water with a constant variation of potential density from top to bottom. Then, if a wind blows over the whole surface with constant velocity, the potential density distribution will come to equilibrium in some such form as in Figure 42, provided there is no non-isentropic mixing. Only the potential density surfaces which reach to the sea surface are distorted, because in the deeper layers there can be no motion and hence no pressure gradient.

Actually the tropical waters are not uniformly stratified. Instead there is a marked *Sprungschicht,* with only weak stratification above and below it. Due to this modification the pressure gradient would

probably decrease on descending through the *Sprungschicht* and vanish at its bottom.

This result does not hold strictly in the case of the equatorial currents, for the wind does not blow uniformly over the whole region in question. But if the currents may be regarded as essentially long (of much greater longitudinal than meridional extent), then in all sections parallel to the equator the potential density distribution must be nearly similar except for vertical displacements of whole isolines. This means that the longitudinal pressure gradient at a given potential density must be nearly the same on all sections. Now, if a

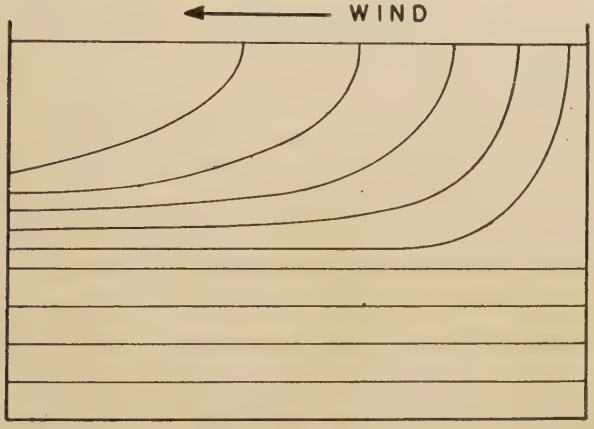

Figure 42. Vertical section of probable potential density distribution in a closed basin under the influence of a constant wind.

longitudinal pressure gradient exists in the deeper layers, it must be locally balanced by the deflecting force on meridional motion, by longitudinal acceleration or by frictional forces on longitudinal motion. The deflecting force vanishes at the equator, and since it has the opposite sense on either side of the equator its net effect on meridional motion must vanish. Any longitudinal motion in the deeper layers would, according to Ekman's theory, be largely a closed circulation contained within the equatorial regions (westward flow in north and south equatorial currents, eastward flow in counter current). Such a closed circulation has no net longitudinal acceleration, and furthermore the sum of the longitudinal frictional forces is probably small. Hence there is still reason to expect the longitudinal pressure gradient to be small or non-existent below the *Sprungschicht*.

Figure 43 shows the σ_t-distribution along the equator, based on the same stations as Figure 39. (The σ_t-values for *Meteor* stations are from Wüst, 1932.) Below 250 meters the isolines show only irregularities, which are probably due to seasonal and other fluctuations. This gives some justification for the assumption in the last section that an isobaric line as shallow as 1000 db is level.

A marked downward slope from east to west extends down to only $\sigma_t = 26.4$, at 100–150 meters depth. Determination of the bottom

TABLE V

σ_t AT *Dana* STATIONS NEAR THE EQUATOR IN THE PACIFIC OCEAN

Depth meters	*3756, 3767, 3775* 134° 44′ E.	*3558* 99° 07′ W.
0	21.68	24.85
10	21.70	24.97
25	21.72	25.16
50	21.90	25.40
75	22.09	25.81
100	22.47	26.16
150	24.32	26.30
200	25.27	26.44
300	26.28	26.57
400	26.80	26.83
500	27.00	27.02
600	27.12	27.06
800	27.30	27.24
1000	27.41	27.40
1200	27.48	27.48

of the *Sprungschicht* is necessarily rather arbitrary, but it appears to coincide roughly with $\sigma_t = 26.4$, so the expectation above is borne out. Also in Table III it was found that the slope of the isobars practically disappears between 100 and 150 meters.

The σ_t-distribution along the equator in the Pacific is shown by Table V. The downward slope of σ_t-lines from east to west extends down to the same σ_t-value as in the Atlantic. In both oceans the slope extends down to the depth where the stability has decreased to a value corresponding to a change of 0.1 in σ_t in about 20 meters, which may be called the bottom of the *Sprungschicht*.

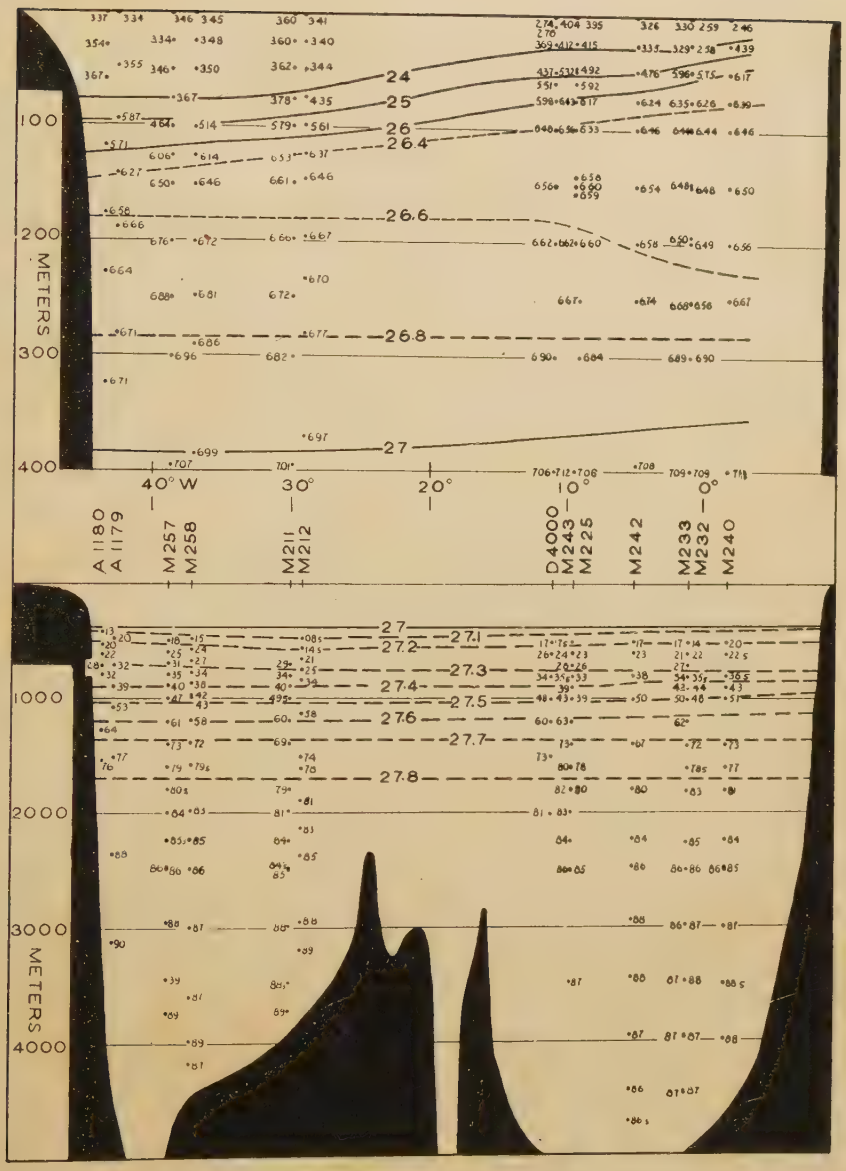

Figure 43. σt-distribution along the equator in the Atlantic Ocean. The exaggeration of the vertical scale with respect to the horizontal is about 10^4 for the upper diagram, about 10^3 for the lower diagram.

4. MAXIMUM ESTIMATE OF LATERAL EDDY VISCOSITY

In the first section the question of the retarding force on the equatorial counter current—whether it is vertical or lateral friction—was discussed without reaching a definite conclusion. Assuming, however, that only lateral friction is of importance, it is possible to estimate the necessary lateral eddy viscosity.

It is assumed that the *Sprungschicht* is contracted to a surface of discontinuity separating resting water below from the lighter and vertically homogeneous water of the counter current above, and that there is no meridional motion. In the longitudinal direction there is balance between the longitudinal pressure gradient and lateral friction. The y-axis is placed northwards, the x-axis eastwards and coinciding with the axis of the counter current. So this balance of forces on unit vertical column, where the upper layer has thickness Z and the lateral eddy viscosity is expressed by η, is written

$$\frac{\partial}{\partial y}\left(Z\eta\frac{\partial u}{\partial y}\right) - Z\frac{\partial p}{\partial x} = 0.$$

In order to integrate this equation easily it is assumed that meridional variations of Z and of η are negligible. If b is the half width of the counter current, integration gives:

$$u = -\frac{1}{2\eta}\frac{\partial p}{\partial x}(b^2 - y^2).$$

Designating the speed in the axis of the current by u_o,

$$\eta = -\frac{1}{2}\frac{b^2}{u_o}\frac{\partial p}{\partial x}.$$

Actually the speed and pressure gradient decrease with depth. Since it is simplest to obtain corresponding values at the sea surface, these will be used in evaluating the last expression. Only the Atlantic Equatorial Counter Current is considered, because less information is available from the Pacific. The slope of the sea surface according to Table III is $3.8\cdot10^{-8}$, so $\partial p/\partial x = -3.8\cdot10^{-5}$ cm^{-2}g sec^{-2} approximately. As the speed of the counter current may be taken the result from dynamic calculation, namely $u_o = 65$ cm sec^{-1} (Montgomery, 1938, p. 19). One means of estimating the width of the current is to take it as half the distance between the axes of low salinity north and south of it on the σ_t-surfaces in the *Sprungschicht* (Montgomery, 1938, Charts 12 and 15). At 40° W., where the speed was estimated, this gives a total width of about 300 km. So $b = 1.5\cdot10^7$

cm. Hence, from the formula above, $\eta = 7 \cdot 10^7$ $cm^{-1}g$ sec^{-1}. This maximum estimate of the lateral eddy viscosity agrees well with the maximum estimate of the lateral eddy diffusivity in the *Sprungschicht* of the Atlantic Equatorial Counter Current, namely $4 \cdot 10^7$ $cm^{-1}g$ sec^{-1} (Montgomery, 1939).

It must be emphasized again that this is only a very rough estimate, which rests especially on the above assumption that vertical friction is unimportant. As was shown in Section 1, this assumption may not be justifiable.

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COMPOSITION OF SEA WATER*

By

JOHN LYMAN AND RICHARD H. FLEMING

Scripps Institution of Oceanography
La Jolla, California

The principle of constant ratios between the salts in ocean water unaffected by land drainage was laid down by Forchhammer in 1864, and firmly established by Dittmar (1884). Dittmar's examination of 77 samples, collected from all the oceans of the world by H.M.S. *Challenger* in 1873–76, was so comprehensive, and his results so consistent, that some of his values are used to this day. Most estimates of the composition of sea water are based fundamentally on Dittmar's work, since subsequent individual investigations have usually been restricted to the determination of one or a few of the major constituents and the establishment of the ratios of these constituents to the chlorinity. In view of the number of such values now available it was considered of interest to prepare a revised table for the composition of ocean water. Also the more accurate methods of analysis now in use make it possible to consider the composition with greater detail. As Dittmar's values have formed the basis of such estimates, it is necessary to consider the effect on his original results of the use of more nearly exact values for atomic weights.

In order to recalculate Dittmar's values with the present accepted atomic weights, the methods by which the various constituents were determined must be taken into account. It is of course implied that the analytical methods were in themselves accurate. Table I compares the atomic weights used by Dittmar with the 1939 International values (Baxter *et al.*, 1939). In the case of potassium, Dittmar used two different values, 39 when computing the results of potassium determinations, and 39.13 when weighing KCl as a standard for chloride titrations. Table II gives the percentage composition of the salts in sea water as reported by Dittmar (1884, p. 203), the factors by which they were calculated from his weighings, and the result of recalculating these percentages with 1939 atomic weights. Dittmar's

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values for calcium oxide and bromine were obtained, not from the entire 77 samples, but from three composite *Challenger* samples and a fourth sample collected near Arran, Scotland. Furthermore, it should be pointed out that sodium was not determined directly, but was estimated by summing the equivalents and calculating the sodium from the deficiency of basic constituents below acidic constituents. Hence any change in the other constituents automatically changes the amount of sodium. Dittmar does not state how he standardized the HCl used in his carbonic acid determinations, but the amount is

TABLE I

Comparison of Atomic Weights

	Dittmar, 1884	*International, 1939*
Ag	107.93	107.880
Ba	137	137.36
Br	79.95	79.916
C	12	12.010
Ca	40	40.08
Cl	35.46	35.457
K	39	39.096
and	39.13	
Mg	24	24.32
Na	23	22.997
O	16	16.0000
P	31	30.98
Pt	198	195.23
S	32	32.06

so small that revised atomic weights would introduce a negligible correction.

A complete analysis of water, for those constituents which bear a virtually constant ratio to the total salt, can be obtained from determination of a single one of these components. It is convenient to refer to these as the *major constituents* of sea water. The major constituent most easy to determine accurately is the silver-precipitating halides, and for this reason the other elements are expressed as a function of chlorinity. Chlorinity, as defined by Knudsen (1902), was the weight in grams (*in vacuo*) of the chlorides contained in one kilogram of sea water (likewise measured *in vacuo*) when all the bromides and iodides have been replaced by chlorides; in other words, the result given directly by the silver nitrate titration. To this definition must be added that the titration results be calculated with the Hydrographical Tables of Knudsen (1901, pp. 23–34) using Copen-

hagen Normal Water as the standard. *It is desirable to maintain an unvarying international standard for chlorinity, independent of atomic weights, in order that the apparent chlorinity of the oceans shall not change as revisions in atomic weights change gravimetric factors.* The Normal Water prepared by the Hydrographic Laboratories of Copenhagen has fulfilled this function. As pointed out by Matthews (Deacon, 1933), all batches of Normal Water have been referred to an original KCl primary standard calculated with 1902 atomic weights; that is, chlorinity as originally defined was identical with the volumetric chlorine-equivalent as calculated with 1902 atomic weights.

TABLE II

PERCENTAGE COMPOSITION OF SEA WATER SALTS AS REPORTED BY DITTMAR, AND AS CALCULATED FROM HIS RESULTS USING 1939 ATOMIC WEIGHTS

	Dittmar, 1884	*Factor used in calculation*	*Dittmar, 1939 atomic weights*
Cl	55.292	Cl/KCl	55.262
Br	0.1884	Br/(Br − Cl)	0.1882
SO_3	6.410	$SO_3/BaSO_4$	6.397
CO_2	0.152	CO_2/HCl · HCl/x	0.152
CaO	1.676	weighed directly	1.674
MgO	6.209	$MgO/Mg_2P_2O_7$	6.237
K_2O	1.332	K_2O/Pt	1.353
Na_2O	41.234	by difference	41.224
	112.4934	Sum	112.4872
	12.4934	oxygen-equivalent of halide	12.4872

Jacobsen and Knudsen (1940) have established a permanent standard for chlorinity identical with the previous one but independent of the store of Normal Water at Copenhagen. The mass of silver required to precipitate completely the halogen in one kilogram of Normal Water of 19.381 ± 0.001‰ chlorinity was found to be 58.9943 ± 0.0008 grams. The new definition of chlorinity is expressed by Cl ‰ = 19.381/58.9943 = 0.3285234 Ag ‰. The 1939 atomic weight ratio Cl/Ag is 35.457/107.880 or 0.328671. Thus the chlorine-equivalent, based on 1939 atomic weights, is 1.00045 Cl ‰. For Copenhagen Normal Water labelled 19.384 ‰ the chlorine equivalent would be 19.393 grams per kilogram. Deacon (1933), as calculated by Matthews, actually found 19.394 as the chlorine-equivalent of such a water, using NaCl as a primary standard, while Thompson and Wirth (1931) found in the same way 19.378 for a water labelled 19.368 ‰ chlorinity.

Table III compares the ratios to chlorinity of the other constituents in sea water of 19.000 ‰ chlorinity as calculated from Dittmar's results in the manner previously explained, with the best values of more recent investigations. The chlorinity in each case has been adjusted to that of Copenhagen Normal Water.

TABLE III

Comparison of Dittmar's Ratios with Present Best Values, and Composition of Sea Water Having Chlorinity 19.000°/₀₀

Ion	*Ratio to chlorinity (Dittmar)*	*Ratio to chlorinity (best value)*	*Authority*	*Equivalents per kilogram*	*Weights per kilogram*
Cl	0.99894	0.99894	Dittmar (1884) and Jacobsen and Knudsen (1940)	0.53529	18.9799
Br	.00340	.00340	Dittmar (1884)	.00081	.0646
SO_4	.1388	.1394	Thompson, Johnston and Wirth (1931)	.05514	2.6486
HCO_3	.00760	.00735	Revelle (1936)	.00229	.1397
F	—	7×10^{-5}	Thompson and Taylor (1933)	.00007	.0013
				0.59360	
Ca	.02163[1]	.02106	Kirk and Moberg (1933) and Thompson and Wright (1930)	.01996	.4001
Mg	.06801	.06695	Thompson and Wright (1930)	.10460	1.2720
K	.02029	.02000	Thompson and Robinson (1932)	.00972	.3800
Sr	—	.000702	Webb (1938)	.00030	.0133
				0.13458	
Na	.5530	.5556	By difference	.45902	10.5561
				0.59360	
H_3BO_3	—	.00137	Harding and Moberg (1933) and Igelsrud, Thompson and Zwicker (1938)		.0260
					34.4816

[1] This ratio of Dittmar's is for calcium plus strontium, determined gravimetrically as oxide. The calcium and strontium best values would be 0.02165 if calculated on this basis.

The ratios for chlorine to chlorinity and bromine to chlorinity have been calculated from Dittmar's bromine : chlorinity ratio, and from the factor 1.00045 just derived. At 19.000 ‰ chlorinity, we obtain 18.9799 grams of chlorine and 0.0646 grams of bromine per kilogram. This bromine is equivalent to $0.0646 \times 35.457/79.916 = 0.0287$ grams

of chlorine, so the total chlorine-equivalent is 19.0086 and the ratio to chlorinity 19.0086/19.0000 = 1.00045.

In order to make it possible to consider the sum of all the constituents of sea water, some of the ratios of other constituents to chlorinity have been carried to a number of figures probably not justified by the accuracy of the procedures by which they were determined. In the following discussion, unless otherwise stated, the units used are grams per kilogram of sea water.

The sulfate : chlorinity ratio for a series of samples from various oceans was found by Thompson, Johnston and Wirth (1931) to be 0.1395; corrected for buoyancy in weighing, this is 0.1394. Revelle (1936) found as the base ratio for surface sea water of the northeast Pacific 0.1235 m.eq./liter per Cl ‰. Using a mean density of 1.025 and *assuming all the base to be in the form of bicarbonate,* we obtain a weight ratio $HCO_3/Cl = 0.0735$. Fluorine in sea water was determined by Thompson and Taylor (1933), who found fluorine : chlorinity $= 7 \times 10^{-5}$.

Thompson and Wright (1930) found 0.02150 gravimetrically for the calcium : chlorinity ratio for water of the northeast Pacific. Corrections for the buoyancy in weighings, a slight revision in the atomic weight of calcium, and the fact that NaCl was used as a primary Cl standard, cancel almost exactly. Kirk and Moberg (1933) found 0.02154 volumetrically for water of the same region, and here again, changes in atomic weights of carbon and calcium cancel. Webb (1938), however, has pointed out that strontium in sea water is chemically indistinguishable from calcium, and leads to a high value for the apparent calcium. With a calcium : strontium ratio of 30 : 1 (Desgrez and Meunier, 1926; Thomas and Thompson, 1932), these calcium : chlorinity ratios become respectively 0.02090 and .02122, their mean 0.02106, and the mean strontium : chlorinity ratio, 0.000702.

A magnesium : chlorinity ratio of 0.06694 is reported by Thompson and Wright (1930). This is subject to the same buoyancy and chlorinity corrections as their calcium ratio and furthermore to a change in the gravimetric factor resulting from a revision in the atomic weight of phosphorus, becoming finally 0.06695. Potassium is extremely difficult to determine in sea water. Potassium : chlorinity = 0.02000 was obtained by Thompson and Robinson (1932, p. 68) as an average of the values in the literature up to their time, and the recent result of Webb (1939) of 0.02009 ± 0.00020 is in good agreement with this. For sodium we prefer to follow Dittmar and calculate sodium as the deficiency of the other positive ions below the negative ions. The result yielded by this method, sodium : chlorinity = 0.5558, compares

well with the recent value of Webb (1939) from direct analysis, 0.5549 ± 0.0010, and is somewhat higher than the average given by Thompson and Robinson (1932, p. 174) of 0.5509.

Boric acid, which we assume not to be ionized in sea water to any appreciable extent, has been determined by Harding and Moberg (1933) and Igelsrud, Thompson and Zwicker (1938). The former found boron : chlorinity = 0.000239 by weight; the latter 0.0223 mg.at./unit Cl ‰, which is 0.000241 by weight; the mean, 0.000240 is equivalent to a boric acid : chlorinity ratio of 0.00137.

Several analyses of north Pacific sea water have recently appeared (Wentworth, 1939; Miyake, 1939). Lack of sufficient information as to the methods of analysis makes it difficult to evaluate the accuracy of these determinations, and we accordingly have not included them in preparing Table III.

The sum of all the major constituents in sea water of 19.000‰ chlorinity will now be considered. Knudsen (1902) defined salinity as the weight in grams (*in vacuo*) of the solids that can be obtained from one kilogram of sea water (likewise measured *in vacuo*), when all the bromides and iodides are converted to chlorides, the carbonates to oxides, and the remainder dried at 480° to constant weight. If we take the values given in Table III and convert the bromide to chloride and the bicarbonate to oxide (Table IV), we arrive at a value of 34.3243 for salinity, as compared with 34.325 derived from Knudsen's equation given below.

TABLE IV

CALCULATION OF SALINITY

0.1397	HCO_3 =	0.0183	O	Total salt	34.4816
.0646	Br =	.0287	Cl		.1573
0.2043		0.0470		Salinity	34.3243
.0470				Salinity from Knudsen's Tables	34.325
0.1573					

It should be emphasized that the ratios just presented hold good only at chlorinities near 19.00 ‰. Knudsen (1901) in fitting a straight line to his nine direct salinity : chlorinity determinations, obtained the expression S ‰ = 0.030 + 1.8050 Cl ‰, which implies that water having a negligible chlorinity still contains carbonates (expressed as oxides) and sulfates to the extent of 0.030 ‰. Hence the ratios of the major constituents to chlorinity depend on chlorinity. An explanation for this is easily found in the well-known observation

that river water contains more carbonate than sulfate and more sulfate than chloride. Since river water likewise contains more calcium than magnesium, and more magnesium than sodium or potassium, it would be expected that the ratios of carbonate, sulfate, calcium and magnesium to chlorinity all increase with decreasing chlorinity.

This has been shown to be true in the case of carbonate by Mitchell and Solinger (1934), but their ratios at low chlorinities are extremely variable. For the sulfate data from the Baltic, corrected for buoyancy, of Thompson, Johnston and Wirth (1931), the method of least squares yields a straight line, $SO_4 = 0.0061 + 0.1391$ Cl ‰. There are no data for magnesium which can be used in this way. For calcium, Gripenberg (1937) has some very interesting results from the Baltic. She shows that four separate water masses can be distinguished in this area on the basis of their calcium : chlorinity relationships. These yield four straight lines for calcium as a function of chlorinity, the constant term ranging from 0.0019 to 0.0226 and the slope from 0.0258 to 0.0204. The two Baltic stations used by Knudsen to determine the chlorinity : salinity relationship are located near some of

TABLE V

CALCULATION OF THE COMPOSITION OF THE AVERAGE BALTIC WATER WITH WHICH THE SEA WATER OF KNUDSEN'S TABLES IS DILUTED

$S = 0.030 + 1.8050$ Cl (Knudsen, 1901)

$SO_4 = 0.0061 + 0.1391$ Cl (after Thompson, Johnston and Wirth, 1931)
Ca $= 0.0154 + 0.02025$ Cl (after Gripenberg, 1937)

$Mg/24.32 + .0154/40.08 = O/16 + .0061/96.06$ ..... (1)
$Mg + 0.0154 + O + .0061 = 0.0300$ ..... (2)

Mg	0.0020	Mg	0.0020	Mg	0.0020	$CaCO_3$	0.0385
Ca	0.0154	Ca	.0154	Ca	.0154	$MgCO_3$	.0017
SO_4	.0061	SO_4	.0061	SO_4	.0061	$MgSO_4$	.0076
O	.0065	CO_2	.0243	HCO_3	.0493		
	0.0300		0.0478		0.0728		0.0478

$Mg = 0.0020 + 0.06684$ Cl ‰ ..... (3)
$HCO_3 = 0.0493 + 0.004755$ Cl ‰ ..... (4)
$\Sigma = 0.073 + 1.8110$ Cl ‰ ..... (5)

Knudsen's equation gives the limiting concentration of salts other than chlorides as 0.030 ‰, the carbonate being weighed as oxide. Limiting values for SO_4 and Ca were found as described in the text. Two simultaneous equations (1) and (2) are now written, the first ionic, the second stoichiometric. Solution of these gives the limiting values for Mg and HCO_3, from which in turn are found (3), (4) and (5).

Gripenberg's stations, and by using her calcium values for these and the ratio already given for 19.000 ‰ chlorinity, the equation Ca = 0.0154 + 0.02025 Cl ‰ can be derived. We are now in a position to calculate the corresponding equations for magnesium and bicarbonate. (Table V).

Having these equations, we can calculate the composition of sea water corresponding to that in Knudsen's *Hydrographical Tables* at any chlorinity, assuming that the ratios to chlorinity of all the other components except these four are constants; an assumption which, even if incorrect, will introduce no significant discrepancy. The total salt per kilogram, Σ, as distinguished from the salinity, S, will be given by the expression, $\Sigma = 0.073 + 1.8110$ Cl ‰. The total salt per kilogram of solvent water, Z, will then be $Z = 1000\,\Sigma/1000 - \Sigma$, or

$$Z = \frac{73 + 1811 \text{ Cl } {}^{\circ}/_{\circ\circ}}{999.927 - 1.8110 \text{ Cl } {}^{\circ}/_{\circ\circ}}.$$

This quantity Z is useful in dealing with the colligative properties of sea water, as Table VI will show. Here are given the values of Z corresponding to even units of chlorinity, the freezing point, τ, of sea water as measured by Hansen (Knudsen, 1903), and the freezing point as calculated from the equation $\tau = -0.05241\ Z$. Hansen's attempt to express freezing point as a function of another property of sea water led to a more complicated equation, namely $\tau = -0.086 - 0.064633\ \sigma_0 - 0.0001055\ \sigma_0^2$.

The ionic strength, a quantity of importance in the thermodynamics of solutions, can likewise be calculated for sea water. The ionic strength, μ, is computed by first multiplying the concentration of each individual ion, in moles per kilogram of solvent water, by the square of its valence, and then taking half the sum of these products (Lewis and Randall, 1923, p. 373). Proceeding in this way, we obtain

$$\mu = \frac{1.47 + 35.92 \text{ Cl } {}^{\circ}/_{\circ\circ}}{999.927 - 1.8110 \text{ Cl } {}^{\circ}/_{\circ\circ}}$$

which may also be expressed in the form $\mu = 0.00147 + 0.03592$ Cl ‰ $+ 0.000068$ (Cl ‰)^2 in the range of concentrations encountered in naturally occurring sea water. This compares favorably with the equation $\mu = 0.020$ S ‰ $= 0.036$ Cl ‰ derived by Buch *et al.* (1932, p. 35) from Dittmar's original analyses.

TABLE VI

TOTAL SALTS PER KILOGRAM OF SOLVENT WATER AND FREEZING POINT

Chlorinity °/₀₀	*Z, total salts per kg.H_2O*	$\tau = -0.05241\ Z$	*τ, measured*
1	1.888	−0.099	−0.099
2	3.709	.194	.195
3	5.537	.290	.290
4	7.372	.386	.386
5	9.214	.483	.483
6	11.062	.580	.579
7	12.917	.677	.676
8	14.778	.775	.774
9	16.646	.873	.871
10	18.521	.971	.969
11	20.403	1.070	1.068
12	22.292	1.169	1.167
13	24.188	1.268	1.266
14	26.091	1.368	1.366
15	28.001	1.468	1.466
16	29.919	1.568	1.567
17	31.884	1.669	1.668
18	33.778	1.779	1.769
19	35.716	1.872	1.872
20	37.662	1.974	1.974
21	39.616	2.076	2.078
22	41.577	2.179	2.181
23	43.546	−2.283	−2.286

DISCUSSION

Since chloride determinations made with sodium or potassium chloride as a primary standard, or made gravimetrically, and calculated with the present accepted values for atomic weights, will differ slightly but measurably from determinations using Copenhagen Normal Water, it is important that the method of chloride determination be adequately described in reporting chemical oceanographic data. Variations in the reported ratios of other components to chlorinity may be caused by this ambiguity in the method used for chlorinity. Likewise the ratios must be reduced to a vacuum basis, in accordance with the definitions of salinity and chlorinity.

TABLE VII

HYPOTHETICAL COMBINATION OF IONS IN SEA WATER

$Cl = 19.00‰$

Salt	*Grams*
$NaCl$	23.477
$MgCl_2$	4.981
Na_2SO_4	3.917
$CaCl_2$	1.102
KCl	0.664
$NaHCO_3$	.192
KBr	.096
H_3BO_3	.026
$SrCl_2$	.024
NaF	.003
Sum	34.482
H_2O to	1000.000

That the ratios of other ions to chlorinity in sea water are not strictly constant follows from the relationship between chlorinity and salinity established by Knudsen. Brackish waters will vary according to the nature of the particular river water with which they are diluted. It happens that water from the Baltic region was selected as the standard type of diluted water in oceanography, and comprehensive tables of its salinity, chlorinity and density relationships worked out. It follows from this that it is not possible, by extrapolation to zero chlorinity of measurements made in natural sea water, to obtain the corresponding property of distilled water, although this has been attempted in the case of refractive index, dissociation constant, and other measurements. It is also incorrect to make electrical measurements in sea water over a range of chlorinity, by diluting a single sample with "a good grade of conductivity water," although this likewise has been done. Samples diluted with distilled water will not correspond in properties to those of water of the same chlorinity from Knudsen's Tables. Furthermore, in any specific locality where dilution by river water occurs water of a given chlorinity will not necessarily have the same properties as water of the same chlorinity obtained by diluting oceanic water with distilled water nor water corresponding to that of Knudsen's Tables.

In Table VII the ions previously presented in Table III are combined as salts. This tabulation may serve as a basic formula for synthetic sea water of chlorinity 19.00 ‰. It should be noted that as only the major constituents have been discussed the so-called plant nutrients and heavy metals are lacking.

Not only must the qualification "in oceanic water unaffected by land drainage" be added to the principle of constant composition of sea salt, but also, the depth at which the sample is obtained must be specified. The nutrient compounds, nitrate, phosphate and silicate, increase with depth to a point where they can no longer be considered infinitesimal, and the decreased pH favors increased solution of $CaCO_3$ from settling organic detritus. It was for this reason that the calcium and base ratios presented in Table III were both chosen from determinations on samples taken from the upper layers in the same area.

SUMMARY

1. Dittmar's values for the composition of the dissolved solids in sea water are recalculated with 1939 atomic weights.

2. If Copenhagen Normal Water is not available, chloride values obtained using a primary Cl standard must be converted to chlorinity. Jacobsen and Knudsen have found the chlorine-equivalent (1939 atomic weights) to be 1.00045 times chlorinity.

3. To correspond to the definitions of chlorinity and salinity, weighings should be corrected to weights *in vacuo*.

4. Modern determinations of the constituent : chlorinity ratios for surface ocean water have been adjusted as given above and compared with Dittmar's values. Since certain of these ratios increase with decreasing chlorinity, the properties of ocean water diluted with distilled water will not agree with Knudsen's Tables. Certain ratios also increase with depth.

5. From these ratios have been calculated a recipe for artificial sea water, and equations for computing total salt per kilogram of sea water, Σ; total salt per kilogram of solvent water, Z; and ionic strength, μ; in terms of chlorinity.

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THE GREAT BAHAMA BANK. I. GENERAL HYDROGRAPHICAL AND CHEMICAL FEATURES

By

C. L. SMITH

Bahamas Sponge Fishery Investigation Department

I. INTRODUCTION

The Bahama Islands are characterized by the presence of thousands of square miles of shallow sea (<5 fathoms) lying between the various islands. The most extensive of these are the Great Bahama, Little Bahama and Exuma Banks (cf. Fig. 44). A certain amount of discussion has arisen concerning these areas, both in relation to their geological formation and to chemical changes taking place in the water. The author has no knowledge, however, of any previous attempt to make systematic hydrographical and chemical observations in these shallow seas. In view of this the cpportunity was taken to make such observations as were possible, with the time and equipment available, while engaged on conservation work in connection with the local sponge fishery. For this purpose a small section of the northern Great Bahama Bank was selected for special study (Fig. 44). All the sea going work was carried out from a 54 foot motor patrol vessel, the 'Basil Blackett,' which has been fitted out for making simple hydrographic observations. Owing to the inadequate laboratory facilities on board ship the analytical work has been carried out at the shore laboratory in Nassau, whenever the nature of the work permitted.

II. THE GREAT BAHAMA BANK

The position of the Bahama Islands and the main ocean channels in relation to Florida and Cuba is shown in Fig. 44. The largest group of islands and banks is that known as the Great Bahama Bank, including Andros Island and several smaller outlying islands and cays. This bank is so irregular in shape that its general outline is best appreciated by reference to Fig. 44 where the 100 fathom line marks the edge.

On three sides it is bounded by deep ocean channels and on the fourth by Andros Island and shallow flats. To the North is the North West Providence Channel varying from 300–600 fathoms in depth, to

the West is the Florida Channel approximately 500 fathoms deep, and to the South the Old Bahama Channel with a depth of from 300 to 500 fathoms. Between the southern end of Andros Island and the Old Bahama Channel the bank is continuous with the Exuma Bank lying on the eastern side of the deep ocean pocket known as the Tongue of Ocean (800 fathoms). The ocean edge of the bank is marked in many places by small cays and a few habitable islands such as the Biminis and the Berry Islands. The transition from the

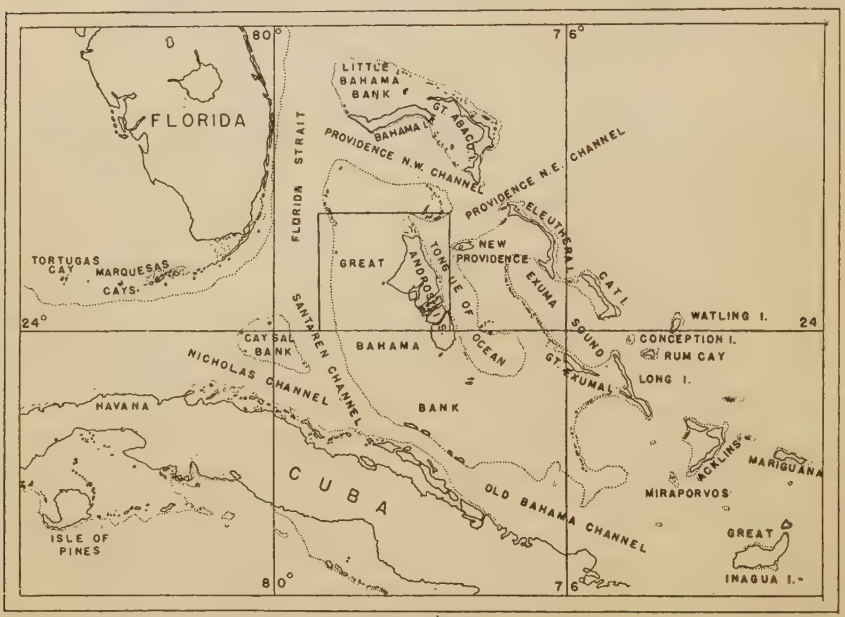

Figure 44. Chart showing relation of the Bahama Islands to neighboring land and ocean channels . . . . . line represents 100 fathom line.

shallow bank to deep ocean is everywhere very abrupt, the five and hundred fathoms lines often being less than a mile apart.

Andros Island, the largest of the Bahama group, is about 95 miles long and varies in width from 18 miles at the southern end to 40 miles in the centre and only 10 miles at the northern end. The formation of the island is oolitic limestone (Vaughan 1914). This rock supports a low vegetation of palmetto scrub with ridges of pine forest, though soil is practically non-existent except in rock holes. Continuous erosion of the calcareous rock is taking place, and in many places it is honeycombed by solution. The topography of the island has been

well described by Drew (1914). Along the eastern side there is a low range of hills about 100 feet high and offshore there is a very well developed barrier reef of coral. The west coast of the island is composed of soft slimy mud and is so low that in northwesterly gales it is overflowed to a considerable distance inland. Offshore the water is so shallow that it is impossible to approach within several miles of the coast in anything but a dinghy boat. The west coast is broken up by numerous creeks which may run inland for considerable distances, giving off branches in all directions, and forming a veritable maze of inland waterways. Some of these creeks are comparatively deep (1 fathom) and they all lead eventually to shallow inland lakes, locally called 'swashes,' which very often contain only a few inches of water and several feet of very soft mud. These lakes are many square miles in area and from the air the west side of the island appears to be largely composed of water. The tidal streams in the creeks are swift and carry down large quantities of mud which forms shallow bars across their mouths and renders access to them difficult.

Andros Island is divided into two main parts by three bights which lead from the Tongue of Ocean on the East to the shallow bank on the West side. These are known as North, Middle and South Bights, although North and Middle Bights are only divided by an archipelago of small cays and communicate freely. At the northern end of the Island an extensive mud flat, dry in many places at low water runs some 12 miles northward. To the north of this flat the contour of the bank forms a deep V-shaped indentation of deep water, at the head of which is a narrow 10 foot channel leading onto the bank (North-west channel).

The low swampy West coast of the island slopes very gradually and is continuous with the shallow submarine flats forming the Great Bahama Bank which extend some 60 miles out to sea. The course of the one, two and three fathom lines is shown in Figs. 46 to 49 and it can be seen that the greater part of the northern bank is less than 3 fathoms in depth, while the one fathom line may lie as far as 5 miles from the shore. The bottom consists of fine calcareous marl composed almost entirely of minute unorganized particles of calcium carbonate. Near the shore this marl is very soft and a 12 foot pole may be pushed down into it in places without striking hard bottom. The greater part of the bottom is very clean there being little living matter with the exception of small rootlets of Zostera. Scattered over the bank, however, there occur patches of rocky bottom and here an abundant fauna is found consisting mainly of gorgonid corals, sponges, Zostera and schools of fish. This bank is one of the richest grounds in the

colony for commercial sponges, most of them being taken from these rocky patches or 'bars,' although many sponges break off from their original attachment and become 'rollers,' when they occur wherever the currents drift them.

Vaughan (1918) gives a very complete description of mechanical and chemical analyses of samples of the bottom deposits in the waters near Andros Island. He found that these deposits could be separated into four main categories:

(a) Sands forming behind the coral reef on the Eastern side of the island. These contained only 1.7% of clay and silt size particles (0.05–0.0 mms.), and were composed largely of remains of organisms. They were characterized by a high magnesium carbonate content (5.24%).

(b) Lagoon deposits forming on the extensive flats protected by land on the windward side. This type was a fine grained oolitic mud (60% clay and silt sizes), light gray in color, with an alkaline reaction. It contained a few shell fragments, fragmental $CaCO_3$ and a few foraminifera. The chemical analysis showed 96.84% $CaCO_3$, 2.72% $MgCO_3$, 0.29% SiO_2 and 0.15% $(Al, Fe)_2O_3$. The depth of this deposit varied from 2–7 feet the underlying material being hard rock.

(c) Oolitic sand formed by the breaking up of indurated oolite by wave action. This type contained only 2–3% of clay and silt sizes and was practically pure $CaCO_3$ (99.5%). In all respects it was identical with the oolite now elevated above sea-level.

(d) Globigerina ooze, covering the bottom of the Tongue of Ocean.

Vaughan found the deposits of type (b) & (c) on the Great Bahama Bank, type (b) being universal close to the western end of South Bight and type (c) at the northern end of the bank (the samples were taken on a W. N. W. course from the North end of Andros to Gun Cay on the edge of the Florida Channel).

Unfortunately Vaughan did not collect any samples from the central part of the bank, nor did he ascertain the total areas covered by each type of deposit.

Thorp (1936) also carried out mechanical analyses of samples of the bottom deposit from the West end of South Bight. His results were essentially the same as Vaughan's. Both observers found many oolite grains in these deposits and also countless minute particles of aragonite. They both reached the same conclusion that this type of deposit is forming by chemical precipitation of calcium carbonate from sea-water.

The author has collected several bottom samples from various parts of the Bank and though no attempt at mechanical or complete chemi-

cal analysis has been made it is apparent that the conditions described by Vaughan and Thorp still obtain in this area. The lagoon deposits of Vaughan are not confined to the entrance of South Bight but extend right along the shore of North Andros and in many cases for a considerable distance offshore. The percentage of clay and silt sizes is probably higher inshore owing to the small amount of water movement. As one proceeds towards the edge of the Florida Channel a mixture of the fine lagoon deposit and oolitic sand is encountered, the oolitic sand proportion increasing as the edge of the bank is approached.

The results of partial analyses of four bottom samples are listed in Table I.

TABLE I

Analyses of Bottom Samples from Great Bahama Bank. For Station Positions cf. Fig. 47. Samples Washed and Dried in Air

Station No.	*Description*	*$CaCO_3$ grs. %*	*Total CO_2%*	*$MgCO_3$ calculated grs. %*	*Total $CaCO_3$+ $MgCO_3$ grs. %*
53	Oolitic Sand	98.2	44.4	2.30	100.5
60	Fine Mud	97.7	44.7	3.26	100.96
49	Fine Mud	95.5	44.7	5.17	100.67
75	Oolitic Sand	98.9	44.4	1.72	100.62

The calcium content of each sample was estimated by standard gravimetric procedure and total carbonate content by heating strongly till constant weight was attained. The latter method is subject to variable errors due to loss of other volatile matter in addition to carbon dioxide, so that the carbonate content observed will be too high. The carbonate remaining after subtracting that present as $CaCO_3$ was calculated as $MgCO_3$. The total $CaCO_3 + MgCO_3$ is slightly in excess of 100% owing to the positive errors mentioned. Estimations of the total organic nitrogen content of bottom samples have been made and were found to vary between 0.12 and 0.04%, the higher values being found in samples taken near patches of Zostera. The four samples shown in Table I can be divided into oolitic sand and fine mud categories by the naked eye. Microscopical examination shows that they all contain oolite grains, though these are fewer and smaller in Nos. 49 and 60. Minute undifferentiated particles and needles (aragonite) are found in abundance in these two samples, though of the two No. 49 is definitely the finer deposit. Nos. 53 and 75 contain many large oolite grains with but a small proportion of undifferentiated fragments and needles (very few of the latter in No. 75). Foraminifera of the *Orbiculina* type are found in all the samples. Of

these samples, then No. 49 from close inshore is the finest with No. 60 from about 25 miles offshore only slightly coarser. No. 53 from near the western edge of the bank is an oolitic sand with a slight but definite admixture of a finer deposit, while No. 75 from the more northern part of the bank is an almost pure oolitic sand.

Bottom samples have also been taken in the shallow lakes inland and they were of essentially the same type as No. 49.

III. WATER MOVEMENTS

The general ocean current system around the Bahama Islands is bound up with the currents forming the sources of the Gulf Stream. The main current is a general westerly drift representing the continuation of the Northern Equatorial Current. The low surface salinities (36.2–36.4‰), however, indicate that water of a southern origin is also being carried up into these latitudes. The Antilles current is the most probable agency in effecting this transportation, although its strength is rather uncertain. The 'Atlantis' observations off Abaco Island (Iselin 1936) showed only a relatively weak current close inshore while the surface water down to 400 metres appeared to be moving southward. The northward flow at mid-depths was presumably stronger, though the resulting movement was relatively small. Iselin, however, points out that the velocity of this current may be greater in the summer months when the trade winds follow the sun northwards.

The currents in the Old Bahama Channel are described in the West Indies Pilot as setting to the North West, but they are weak and readily influenced by the wind. The same authority describes the currents in N.E. Providence Channel as being variable, while in N.W. Providence Channel there is generally but little current except after northerly winds when it may set eastward with a velocity of 1 knot. It must be remembered, however, that the West Indies Pilot refers only to observed currents in the surface layer and it is most probable that at mid-depths in all the above channels there is a steady westerly drift, the varying wind currents being super-imposed on this movement. The Florida Channel, of course, contains the main axis of the northbound Gulf Stream. The width of the Gulf Stream is variable and at times it strikes full on the Great Bahama Bank about latitude 25° 30′, though generally it lies farther offshore. The 'Atlantis' observations North of Cape Hatteras have sometimes shown the presence of strong counter currents along the southern edge of the Gulf Stream (communication from Dr. H. B. Bigelow) and it is probable that similar currents may develop along the outer edge of the current

in the Florida Channel as the result of short period changes in its strength. In view of this it may be that the deep water immediately offshore from the Great Bahama Bank has a southerly movement at times.

Due to the peculiar relation of the Great Bahama Bank to neighboring land masses and deep ocean channels the tidal streams running on and off the bank tend to be complex. Near the edge of the bank the tidal direction is roughly at right angles to the 100 fathom line and the strength varies from 1 to 2 knots, but in the central region the opposing streams tend to meet and produce a resultant tidal flow. Thus, on the Northern part of the bank, the tide from the Florida Channel has an East-West, while that from the Providence N. W. Channel has roughly a North-South direction. Where these two streams meet the tide may be observed as flooding towards the South East and ebbing towards the North West. With increasing distance from the Providence N.W. Channel the influence of the North-South components becomes less and less and in about latitude 24° 20′ N. the tide floods toward E. by S. On the Southern edge of the bank the tide floods to the North from the Old Bahama Channel and the central part of the Southern bank has a tidal set towards N.E. owing to an interaction similar to that described above. The tidal rise and fall over the whole area is small being about 3 feet at ordinary spring tides on the edge of the bank and decreasing on the central and inshore areas.

When considering the chemical changes taking place in the water on the bank it is more important to know the direction and extent of the daily water drift (residual current) rather than the tidal movements. For this purpose several observations have been made on the Bank with a Carruthers' Drift Indicator (Min. Agri. Fish. Notice No. 17). This instrument shows the daily residual current after the opposing tidal influences have been cancelled out. Table II shows the records obtained with the instrument and the average wind conditions during the period of the observations.

The most extensive series of observations was made in December 1939, during a period of very light winds. Under such conditions the residual current over the central part of the area is approximately 1 mile per lunar day towards S.E. Inshore the current tends to be weaker (0.5 miles/day at St. 125) and more easterly. Although the wind was very light throughout the cruise, the resultant wind force over the period Dec. 1st–14th was computed as a 3 m.p.h. wind from N.N.W. A single current meter observation was made on Jan. 17th 1940 at approximately the position of station 125 (St. 137), when the resultant wind force was 2.5 m.p.h. from N.E. x N. On this occasion

TABLE II

CARRUTHERS' DRIFT INDICATOR OBSERVATIONS. RECORDS FROM GREAT BAHAMA BANK ARE SHOWN GRAPHICALLY ON FIGS. 46 AND 49

Position & Date	*Total daily water movement nautical miles*	*Duration of observations lunar days*	*Residual Current Miles per lunar day*	*Direction*	*Wind Average Force*	*Average Direction*
Great Bahama Bank						
17: 9: 38 Stat. 28	7.2	1	2.0	W. x S.	6 m.p.h.	S.E.
4: 12: 39 Stat. 113	8.6	2	1.0	S.E.	Light Airs	Variable
6: 12: 39 Stat. 116	5.0	1	0.3	S.E. x S.	Calm	
7: 12: 39 Stat. 119	3.0	1	0.9	S.E.	Light Airs	N.W.–N.E.
9: 12: 39 Stat. 121	3.0	1	0.8	S.E. x E.	Light	N.–N.E.
10: 12: 39 Stat. 125	1.3	1	0.5	E.S.E.	Light Airs	N.W.–N.E.
12: 12: 39 Stat. 127	3.5	2.	0.9	E.	4.5 m.p.h.	N. x E.
17: 1: 40 Stat. 137	1.7	1	0.6	S.W.	2.5 m.p.h.	N.E. x N.
Andros Middle Bight						
28: 2: 37.....	12.8	2.	2.5	S.E.	Fresh	S.W. to N.
5: 3: 37	7.5	3	2.1	W. x N.	Light to moderate	S.E.
28: 4: 37	12.3	3	1.9	W. x N.	Fresh	E.N.E.–E.S.E.
1: 5: 37	13.5	3	0.4	S.E. x S.	Moderate	W.

the residual current was 0.6 miles/day towards S.W. This indicates very strongly that the sluggish currents over the shallow bank are controlled very largely by wind action. Confirmation of this is provided by another single observation on Sept. 17th 1938, when the resultant wind for the period Sept. 10th–18th, was 4.5 m.p.h. from E.N.E., and the residual current was 2.0 miles/day towards W. x S. Similarly the four observations in the Andros Bight shown in Table II, indicate a similar reversal of the current due to wind action. With a westerly wind the water flows from the bank to the Tongue of Ocean and in the opposite direction with an easterly wind.

This dependence of the residual current on wind action enables one to follow the main seasonal changes by studying the yearly wind records from the Bahamas. In Table III, the number of days per month on which the wind blew from various directions is shown for the year 1939.

TABLE III

Showing Wind Direction in Number of Days per Month During 1939 From Nassau Meteorological Station Records

Month	*N.*	*N.E.*	*E.*	*S.E.*	*S.*	*S.W.*	*W.*	*N.W.*	*Calm*
January	3	6	5	7	1	1	0	2	6
February	1	7	4	12	1	2	0	0	1
March	1	9	7	10	2	1	0	0	1
April	1	5	5	11	3	3	1	1	0
May	3	3	6	10	3	5	0	0	1
June	0	4	8	10	2	1	1	1	3
July	0	0	5	14	5	5	0	0	2
August	0	3	7	12	3	4	0	0	2
September	1	7	2	7	2	1	0	0	10
October	0	21	4	1	2	0	0	0	3
November	6	12	3	3	1	0	1	4	1
December	5	5	5	5	2	2	0	7	0

These records show that a rough distinction between summer and winter phases can be drawn. In the summer the wind blows largely from the S.E. and E., owing to the effect of the trade wind belt moving northward. In the winter, however, the influence of the trades is less and the winds become more variable with an increasing northerly component, the end of the summer phase being usually characterized by a series of fresh N. westerly winds which cause a sharp fall in air temperature. To illustrate this seasonal change in wind direction the resultant force and direction of the wind for the months of July and December 1939 has been computed from the daily records kept by the Nassau Meteorological Station. In July the resultant wind action was equivalent to a 3 m.p.h. wind from the S.E., while in December the direction was N. by E. and the velocity 2.4 m.p.h., showing a shift of 125° to the North.

In the summer the predominating south easterly winds will result in a steady westerly current across the central part of the bank. The variable and more northerly winds of the winter months will cause a southerly drift, and during the periods of north-westerly gales water will be transported in an easterly direction from the Florida Channel towards the Andros coast. The nature of the current system deduced from these direct observations and wind records is clearly confirmed

by the patterns of the isohaline charts which will be discussed in the next section (Figs. 46 to 49).

The column in Table II, showing the total daily water movement at each station is of interest, as it shows the very quiescent nature of the Bank. Thus at Station 113 towards the northern edge of the bank the daily movement is only 8.6 nautical miles while at Station 125 in the wide bay formed by the shore of Andros Island it falls as low as 1.3 miles. This, of course, represents the minimum movement during a period of light winds, and with a fresh wind it will probably increase. For example, at Station 28 with a fresh S.E. wind, 7.2 miles of daily movement was recorded, while at Station 119, in approximately the same position, only 3.0 miles was recorded in calm weather. The semi-static state of the water which is a product of the opposing tidal influences discussed above and the sheltering effect of the land masses to the East, favors the development and maintenance of hydrographical properties very different from those shown by the surface water of the open ocean. With the prevailing drift observed in December, 1939 water coming onto the bank from the Florida Channel would take at least two months to reach the shore of Andros Island, although such conditions would never obtain for so long a period. Even with the 2 miles per day westerly drift observed with a fresh S.E. wind it would require one month of such drifting to move a body of water from close inshore out into the Florida Channel. As the winds are regularly shifting it is therefore apparent that once a body of water drifts on to the bank it may be shifted to and fro by conflicting wind influences for a long period without making much mileage in any one direction.

IV. DISTRIBUTION OF TEMPERATURE AND SALINITY

(a) *Temperature:* Unfortunately it has not been possible to record the daily temperature of the water on the Bahama Bank so no information is available as to the seasonal variation of the average temperature beyond that yielded by the temperatures recorded when water samples were being taken. Daily records of water temperature have, however, been kept at a field station in the Middle Bight of Andros. The water in this area is in closer communication with the ocean and the tidal movement is greater than on the central part of the bank and hence the records are not strictly applicable to the bank water, but they are sufficiently so to show the nature and extent of the seasonal temperature changes.

In Fig. 45 the average water temperature at 8 a.m. for each month during 1939 based on daily observations, is compared with the average

monthly maximum and minimum air temperatures for the same year recorded at the Nassau Meteorological Station. It is apparent that the water temperature follows the air temperature very closely. Both air and water heat up rapidly between May and June and there is an equally sharp fall in temperature between October and November. The maximum average water temperature (29.7° C.) is reached in August (individual maximum 30.5° C.) and the minimal value (21.6°

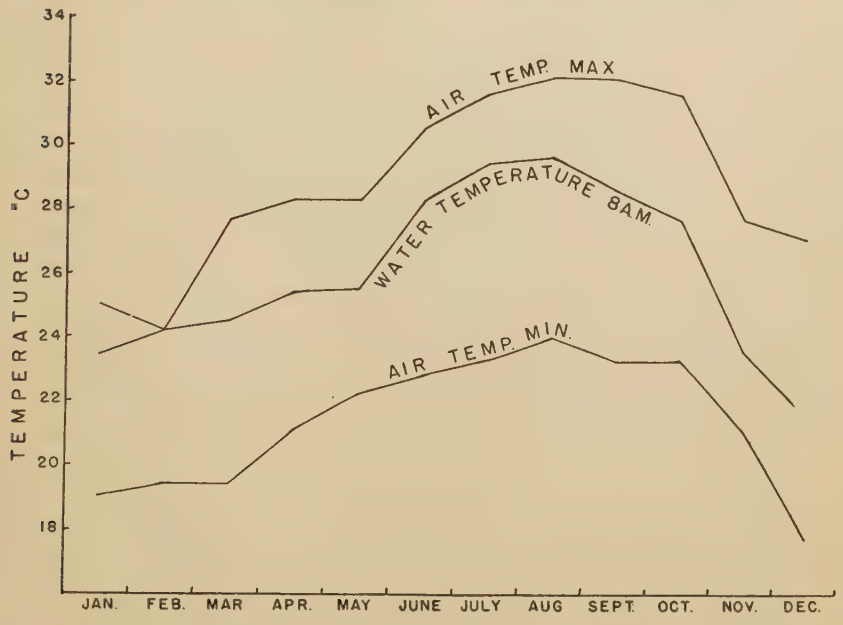

Figure 45. Monthly mean air and sea temperatures based on daily records at the Nassau Meteorological Station. Sea temperatures based on daily observations in Middle Bight, Andros, at 8 A.M.

C.) in December (individual minimum 19.5° C.). The average temperatures recorded for the bank water over short intervals during the same year agree fairly well with the average values for the Bight water with the exception of a temperature of 30.0° C. recorded over a 10 day period in early October. This observation is 1° higher than the average September value in the Bight and 2° C. higher than that for October. It may well be, therefore, that the maximum temperature was maintained till later in the year on the bank. Temperature observations of the surface water in the ocean have not been observed frequently enough to permit the tabulation of monthly values. The

observations show, however, that the ocean attains its maximum surface temperature in October (28–29° C.) and reaches minimal values about February (23° C.). This lag of the ocean temperature behind that of the bank water was shown very clearly in December 1939 when the ocean surface temperature was 25.0° C. and the average bank temperature had already fallen to 21.4° C.

The distribution of temperature at any one time over the bank is very uniform both horizontally and vertically. The water is too shallow and mixing by wind action too thorough for any vertical stratification to be set up. Significant variations in horizontal distribution have only been observed close to the edge of the bank when the ocean temperature differs appreciably from that of the shallow water. At such times, with a flood tide, the influence of the warmer or cooler ocean water can be detected up to a distance of 5 miles from the edge of the bank. Observations of the diurnal temperature range on the bank show that it is of the order of 1° C. throughout the year, and subject to very little seasonal variation.

(b) *Salinity:* The distribution of salinity over the northern part of the Great Bahama Bank during Sept. 1938, and April, October and December 1939 is shown in Figures 46, 47, 48, and 49 respectively. It is readily apparent that the charts for September, April and October present a roughly similar pattern, while that for December is of a very different type.

The first pattern is characterized by the occurrence of very high salinity water lying close to the shore of North Andros Island, the maximum value being >43 ‰ in September 1938 and April 1939. From the position of the salinity maximum the isohalines push out like a wedge, between the lower salinity water to the North and South, towards the Florida Channel. The apex of this wedge lies constantly fairly close to the 25th parallel of latitude. In Fig. 46 there is distinct evidence that the apex of this wedge of high salinity water is being pinched off by an invasion of less saline water from both sides, while a similar process is probably beginning in Fig. 47. In September and April there is a zone of very rapid salinity change close to the edge of the bank. This is shown clearly in Fig. 46 but not in Fig. 47 as the high salinity water extended beyond the edge of the bank (where the salinity was >39 ‰) and outside the range of the samples. In the latter case the transition zone was probably sharper than in Fig. 46 as dilution by surface ocean water would be very rapid. Another zone of extremely sharp salinity change occurred in Sept. 1938 (Fig. 46) at the northern end of Andros Island, where the salinity fell 3 ‰ in a distance of five miles. The salinity change in this area was

more gradual in April 1939, though there is a secondary transition zone farther South, lying between stations No. 47 & 71. In October 1939 the transition zone between the bank water and the ocean in the Florida Channel was broader though still quite clearly defined,

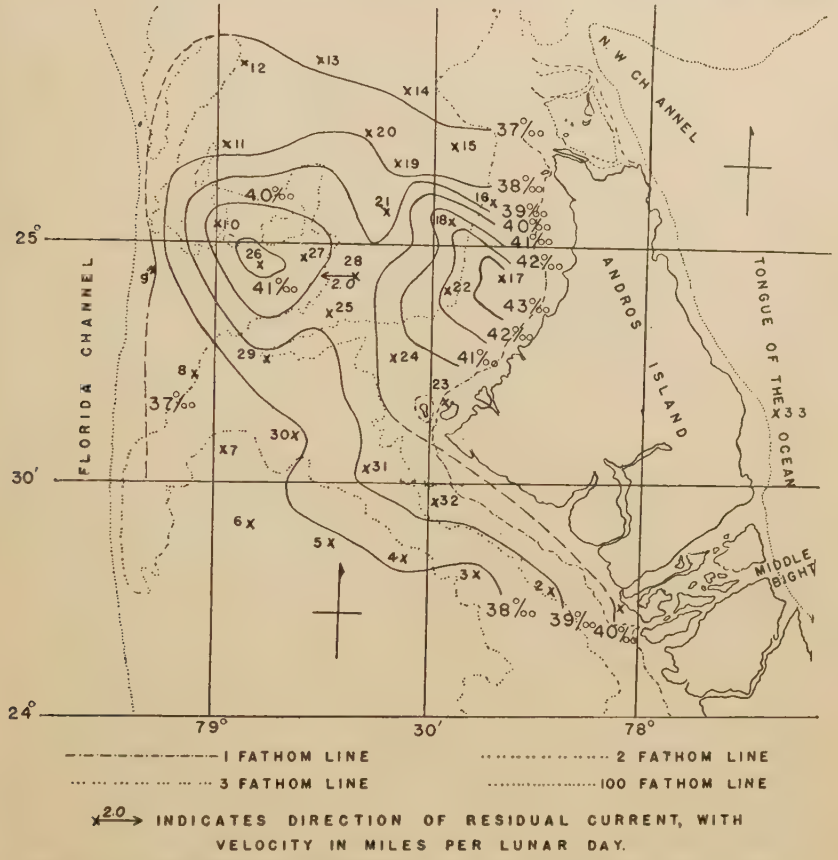

Figure 46. Showing distribution of isohalines over part of the Great Bahama Bank during period of Sept. 15–18, 1938. Resultant wind Sept. 10–18 = 4.5 m.p.h. from E.N.E.

and again there is a sharp transition zone near the northern end of the island. On the southern side of the high salinity wedge the salinity changes tend to be more gradual on all three cruises. There is again a narrow belt of high salinity water close inshore but the salinity falls regularly with increasing distance offshore and in September and October at least there was no sharp transition zone on the edge

of the bank in latitude 24° 30′. Conditions in April were somewhat different as water >39 ‰ occurred over all the southern part of the area and a sharp zone of salinity change probably did occur in this latitude just beyond the edge of the bank. This marked westerly extension of high salinity water in April is due to strong easterly winds,

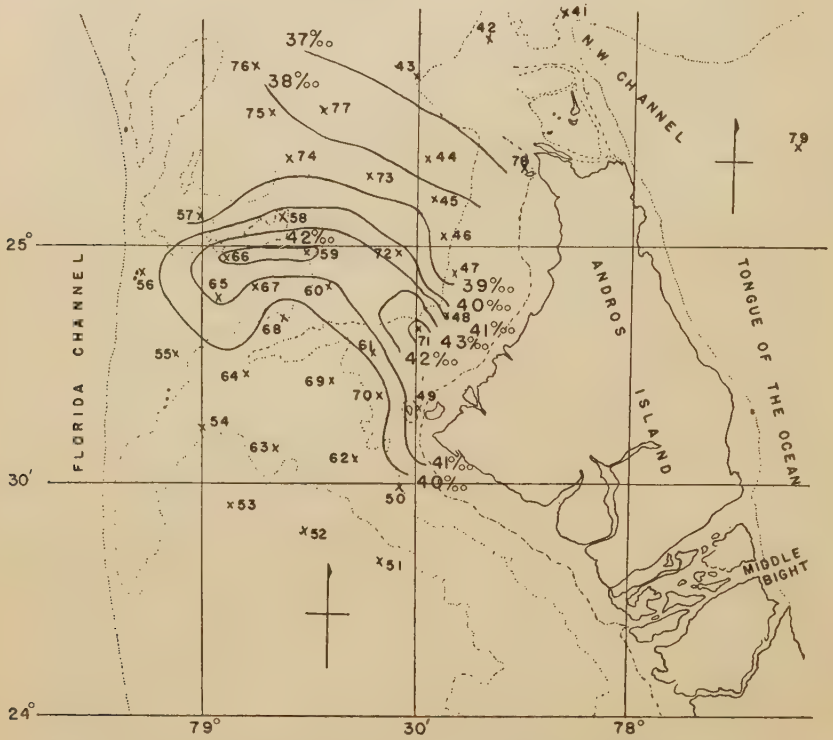

Figure 47. Showing distribution of isohalines over part of the Great Bahama Bank during period of April 18–22, 1939. See legend Figure 46. Resultant wind April 10–22 = 8 m.p.h. from E.

the resultant wind for the period April 10th–22nd, being 8 m.p.h. from the East.

In December, 1939 (Fig. 49) the pattern of salinity distribution is very different from the above. With the exception of Station 127 (38.24 ‰) the salinity over the whole area is <38 ‰. At Stations 130 & 129 there is also evidence of dilution by fresh water. This is probably caused by land drainage from the North and Middle Bights where salinities <23 ‰ were recorded in early November after a

period of heavy rain. The 37 ‰ isoline on this cruise showed a somewhat irregular distribution, moving westerly towards the Florida Channel at Station 122, but there is no evidence of the high salinity wedge so characteristic of the other cruises.

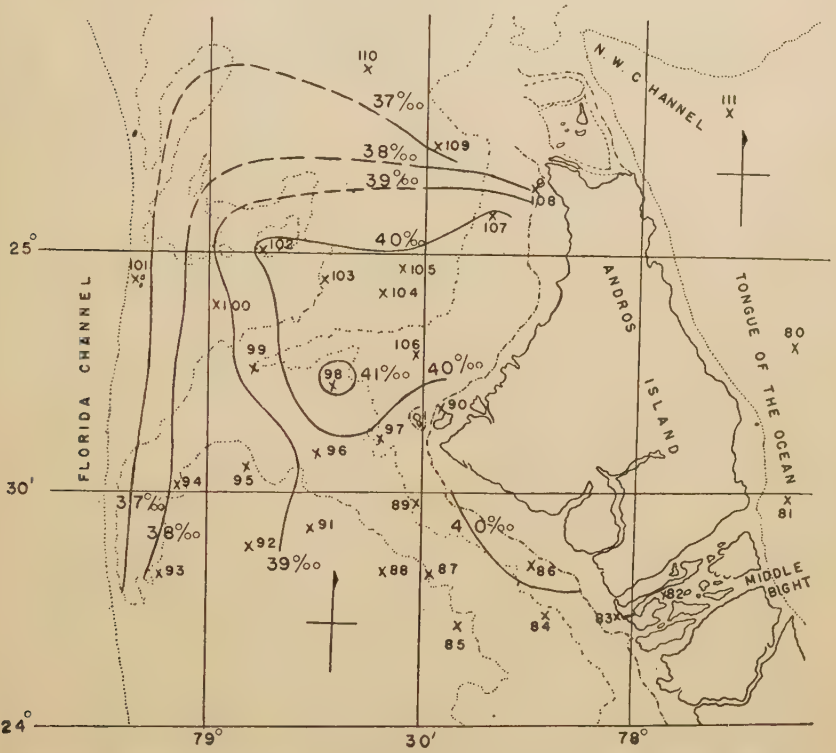

Figure 48. Showing distribution of isohalines over part of the Great Bahama Bank during period of Sept. 29—Oct. 8, 1939. See legend Figure 46. Resultant wind during period = 5 m.p.h. from N.E.

The broad outlines of the current system on this bank have already been described and evidence presented showing that seasonal changes are to be expected. Such a concept makes the salinity charts readily intelligible. Thus in September, April & October (Figs. 46, 47 & 48) the main current is towards the West or North-West and it is obviously carrying high salinity water from the inshore area out towards the ocean. As this water is transported westward there would be a tendency for the lighter water ahead and on both sides to flow over

it, but this is prevented by the frictional force of the wind, so that mixed water does not appear in any quantity.

In December the observed drift at several stations (shown on Fig. 49) had a definite easterly component, so that low salinity water from the ocean is being carried across the bank towards the land. The

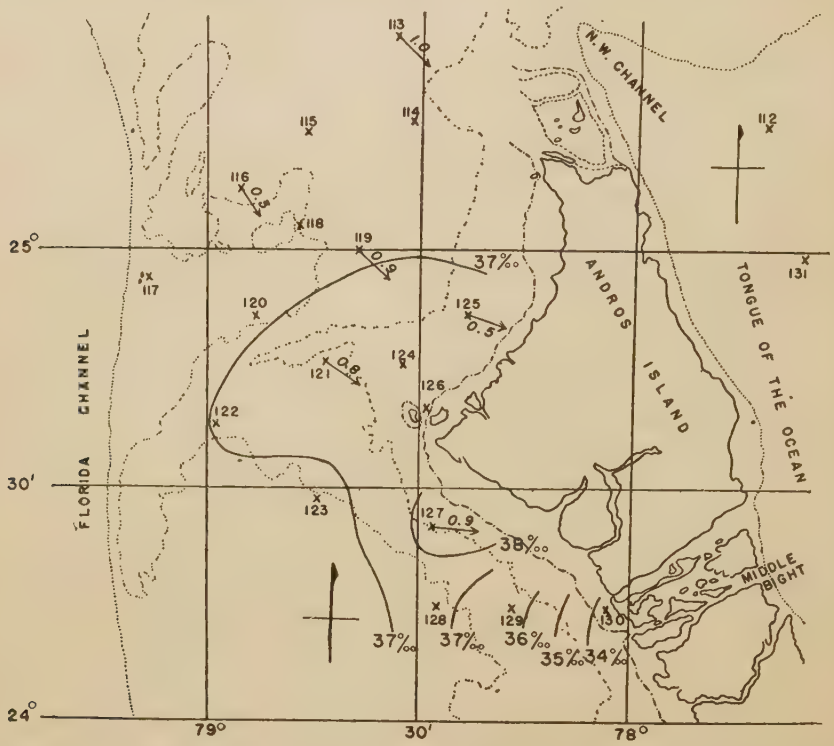

Figure 49. Showing distribution of isohalines over part of the Great Bahama Bank during period of Dec. 4–14, 1939. See legend Figure 46. Resultant wind Dec. 1–10 = 3 m.p.h. from N.N.W.

slight increases in salinity observed are due to a combination of two factors. In the first place even in the winter months some evaporation of the water in its slow progress across the bank takes place. Secondly high salinity water is continually spreading on to the bank from the shallow lakes on the west coast of Andros by tidal action. This latter effect may be considered in greater detail with the aid of salinity observations made in one of the creeks. Figure 50 shows the salinity changes over a complete tidal period at an anchor station in Deep Creek in January 1940.

At low water high salinity water from the lakes inland appears in the creek, while on the flood tide the lower salinity bank water flows in, until at high water the salinity is the same on the bank and in the creek. Considerable admixture of these two bodies of water must take place on every tide and there will be a tendency for the salinity of the bank water outside the creek to be raised. This tendency must be more pronounced in the summer when the general current is westerly. In addition there will then be a high rate of evaporation from

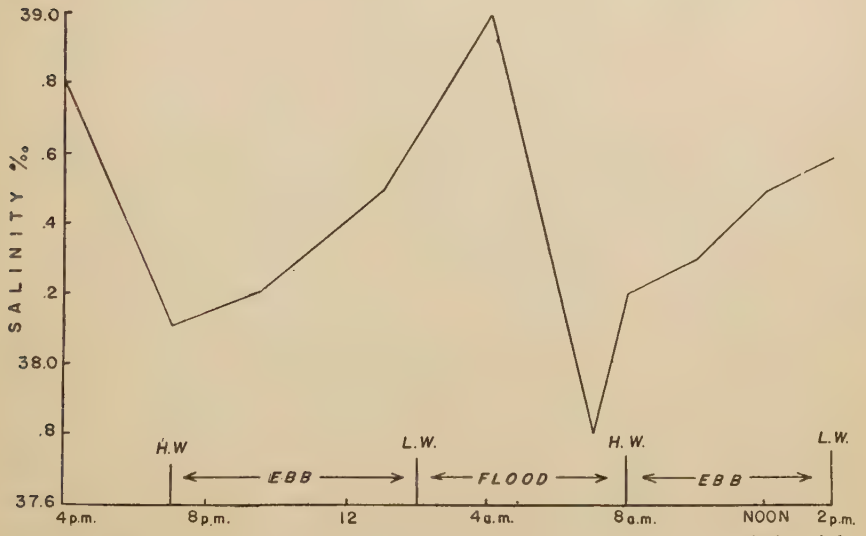

Figure 50. Salinity at an anchor station in Deep Creek, N.W. Andros over a tidal period. Jan. 17–18, 1940.

the surface of the bank water itself. If the sluggish nature of the currents on the inshore part of the bank is borne in mind, it is not difficult to realize why such high salinities are found in this area. The direction of the coastline of North Andros assists the development of extreme salinity values offshore by affording shelter from the prevailing winds. Farther South where the shore runs from N.W. to S.E. the maximum salinity recorded is less than 41 ‰.

If, as shown above the high salinity water on the northern part of the bank is slowly moving westward in summer there must be a slow drift into the area to replace this water. It is suggested that this water flows in from the northern end of Andros Island, and to a certain extent from the inshore area farther south. The extreme sharpness of the salinity transition zone at the northern end of the island

would indicate that the mixed water is being carried away by a weak current running parallel to the isolines. Between stations No. 16 and 18 (Fig. 46) the density (σ_T) decreased from 26.8 to 24.2 over a distance of five miles. The internal dynamic forces in this zone would be great enough to establish a current in opposition to the wind force. Such currents are known to occur in coastal regions where two bodies of water of contrasting density are in juxtaposition. The sharp density transition zones at the apex of the wedge of high salinity water may also be characterized by eddy currents of a similar nature.

V. HYDROGRAPHIC DATA

During 1938 a series of deep sea hydrographic observations were made at a station in the Providence Channel (77° 21′ W., 25° 16′ N.). These observations were unfortunately interrupted by a mishap to the research vessel which disabled her for a long period. A typical hydrographic record for this station is shown in Fig. 51, where temperature, salinity, pH_w, oxygen content and phosphate content are plotted against depth of the sample. The depth was recorded by means of a metre wheel and when the wire angle was $>10°$ a correction has been applied. Owing to the limitations of a small vessel and slow hauling gear the greatest depth sampled was 1250 metres. This depth is sufficient to reach below the main thermocline and penetrate the more homogeneous deep water.

The section shown in Fig. 51, is fairly representative of all the records apart from seasonal variations in the upper 200 metres. The temperature observations show a surface layer down to 100 metres where vertical mixing is sufficient to maintain a homogeneous condition. In the summer, when calmer weather obtains this homegeneous layer shows considerable contraction. Below the surface layer, the thermocline layer extends down to 1,000 metres (taking the 5° isotherm as the lower limit of the thermocline), and the deepest sample enters the upper limit of the deep water layer. Observations during the summer show the presence of a secondary thermocline immediately below the surface layer. The salinity section corresponds fairly closely to the same pattern, the lower limit of the halocline also lying close to 1,000 metres and a maximum salinity of 36.60 ‰ occurring at 150 metres.

The curve for percentage saturation with oxygen shows an oxygen 'poor' layer ($<60\%$ saturation) lying between 600 and 830 metres, below which depth it increases continuously to 1,200 metres. This may be regarded as typical for the ocean water in this latitude (Sei-

well, 1934), as the oxygen minimum lies close to the 10° isotherm and well within the main thermocline.

Considerable variation in the thickness of the oxygen poor layer has been observed at this station (460–900 metres in April 1938) but

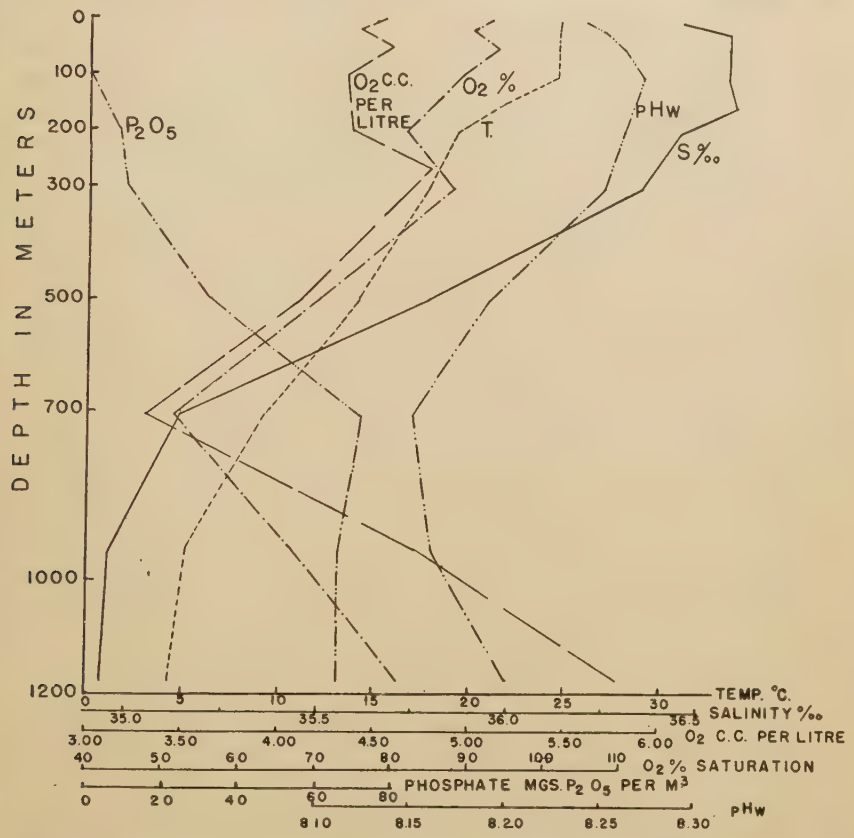

Figure 51. Showing the hydrographic conditions in Providence Channel on Dec. 30, 1938. Station I, 77° 21′ W.—25° 16′ N.

the mean position and relation to the thermocline are fairly constant. Fluctuations in oxygen content appear in the surface layer, due to photosynthesis and respiration. The oxygen saturation in this layer is approximately 90% in the winter months, but supersaturation was found at 10 metres in April and such values are probably characteristic of the summer period. pH_w increases from 8.24 to 8.27 in the

surface layer, then falls steadily to 8.15 at 700 metres, and rises again to 8.20 at 1,200 metres.

In the surface layer phosphate is practically undetectable, but below this it increases steadily to a maximum of 70 mgs. P_2O_5 per cubic metre at 700 metres.

Owing to possible inaccuracies in the recorded depth of the samples it is difficult to compare the several observations at this station directly. For this purpose use has been made of the temperature-salinity correlation method. The standard curve adopted for comparison is that given by Iselin (1936) for the 'Atlantis' stations in the deep water off Elbow Cay, Abaco (Nos. 1476–1478). Table IV, shows the salinity departures from the standard curve for three observations in the Providence Channel and one station off Elbow Cay, Abaco. The salinity anomalies were read off horizontally, a positive sign being given to points to the right of the standard curve and vice versa. The depths given are those recorded for these observations and do not correspond with the depth scale on Iselin's curve.

TABLE IV

Showing Salinity Anomalies (pts./100,000) for Stations in Providence Channel and off Elbow Cay, Abaco. T–S Curve for Atlantis Stations 1476–1478 Used as Standard (off Elbow Cay, Abaco). (Iselin (1936))

Depth (Metres)	*Station 12 miles North from Nassau, N.P. in Providence Channel. Depth 2,800 m.*			*Station 10 miles East from Elbow Cay, Abaco. Depth 1,000 m.*
	5: 1: 38	30: 4: 38	30: 12: 38	30: 11: 37
200	0	−12	−16	+3
300	−6	−14	−11	−6
500	−4	+2	−11	−5
750	—	+11	−7	−5
1,000	−3	+20	−6	−2
1,250	0	+20	−6	

The observations off Elbow Cay on 30th November, 1937 correspond fairly closely with the standard T–S curve, showing negative anomalies at mid-depths. The Providence Channel station, however, shows considerable variation, both in the different observations and in comparison with the Elbow Cay T–S curve. The mid-depths in December and January 1938 show negative anomalies (more marked in December), while high positive anomalies occurred in April at from 750 metres to 1,250 metres depth. It is possible that these changes are due to variation in the influence of the high salinity

Mediterranean water and low salinity sub-Antarctic intermediate water (cf. Iselin 1936).

The depth scale for the T–S curve in the Providence Channel departed considerably from that off Elbow Cay. The Elbow Cay observations agreed fairly closely with the depth scale for the 'Atlantis' stations, the only discrepancy being a slightly higher level of the isolines between 300 and 750 metres. The Providence Channel observations, however, all show considerable elevation of the isolines, especially between 300 and 750 metres where in several cases they are 200 metres nearer the surface than off Elbow Cay. Iselin (1936) observed that at the two most eastern stations in a section across the Gulf Stream off Cape Canaveral water characteristic of the Antilles Current at 500 metres appeared at 300 metres. In view of the elevation of the isolines found at this Providence Channel station it may be that the water found by Iselin at these Gulf Stream stations represented Antilles Current water which had joined the main Gulf Stream after passing through the Old Bahama or Providence Channels.

Hydrographic stations have also been occupied in the remarkable ocean pocket, known as the Tongue of Ocean, lying between New Providence and Andros Islands. The temperature and salinity sections for this area show no significant departure from those in the nearby Providence Channel.

The relation between the temperature and salinity of the shallow water on the Great Bahama Bank and the surface water in the ocean has already been mentioned, and other chemical differences will be described in a subsequent paper. It may, however, be noted that the phosphate content of the shallow water, like that at the ocean surface is practically undetectable, although a few observations in winter showed about 2–3 mgs. P_2O_5 per m^3. Silicate content is also low (100–150 mgs. $SiO_2/m.^3$ in winter) with a tendency to be lower on the bank than in the ocean. Silicate content of the bank water must be largely controlled by the presence of a large sponge fauna on the bottom, several species having a skeleton composed of siliceous spicules. A slight seasonal change in the oxygen content of the shallow water has been observed on the bank, due to the increased temperature and photosynthetic activity in the summer months. In general the water is 96–100% saturated with oxygen in December, while in April 107–118% saturation occurs. No observations are available to show the maximum degree of supersaturation attained in mid-summer.

VI. METHODS

1. *Sampling.* The water samples for the deep sea hydrographic stations were taken in a Nansen-Petersen water bottle with paired reversing thermometers attached so that they reversed when the bottle closed. The bottle was suspended on 3 mm., steel wire rope and was hauled up by means of a hydraulic capstan on the deck of the vessel. The amount of wire run out was recorded on a metre wheel, and corrections made for wire angles $>10°$. Owing to the shallow draught of the boat and her relatively large wind area, it was only practicable to work stations in light weather, as otherwise the drift while working a station was found to be too great.

Water samples on the Great Bahama Bank are spot samples taken about 1 foot below the surface. Previous observations have shown that there is no difference between surface and bottom samples in such shallow water. All water sample bottles were of standard Marine Biological Association pattern.

2. *Temperature.* Deep sea temperatures were all recorded by reversing thermometers. These were used in pairs to guard against errors developing in one of the instruments. The temperature of shallow water samples was taken by direct observations on the sample when taken. These readings were usually checked by using reversing thermometers from the side of the vessel.

3. *Salinity.* Salinity was estimated by titration with silver nitrate. The silver nitrate was frequently standardized against International Sea Water and titrations were made in duplicate. The salinity results are considered to be accurate within ± 0.02 ‰ Cl.

4. *Oxygen.* has been determined by the standard Winkler method. In deep sea work the samples were drawn off directly from the Nansen-Petersen bottle, while in shallow water a special sampling bottle was used to ensure that the sample did not come in contact with the atmosphere. The Winkler reagents were added on board ship when the sample was taken. Fox's table (1907) has been used for calculating the percentage saturation at the temperature and salinity observed at each station.

5. *Phosphate.* was estimated by Atkins' modification of Denigès method (Atkins 1923 (1)). The comparison with standard solutions was made in Hehner tubes and a blank correction applied for the blue color of sea water and for impurities in the reagent (Cooper 1933). The results have not been corrected for salt error.

6. *Silicate.* was estimated by Diénert and Wandenbulckes' method. (Atkins 1923 (2)).

VII. SUMMARY

1. A general description of the topography and bottom deposits of the Great Bahama Bank is given.

2. It is shown that the water movement over the bank is primarily controlled by the direction and velocity of the wind. The seasonal changes in the wind system in the Bahamas are discussed and the consequent effect of such changes on the current system. Drift Indicator observations show the quiescent nature of the water mass and its suitability as a region where the chemical changes taking place in the water of shallow tropical seas may be investigated.

3. Charts are given showing the seasonal distribution of salinity over part of the Bank. In the summer very high salinities occur inshore (>43 ‰), and owing to the westerly drift a wedge of high salinity water extends almost to the edge of the Florida Channel. In the winter, weather conditions are not favorable to the development of this system. The origin of this highly concentrated water is discussed in relation to the system of creeks and extensive shallow lakes which is found on the West coast of Andros Island.

4. Observations made at a deep sea hydrographic station in the Providence Channel are briefly discussed. The character of the water at mid-depths suggests a Northern Equatorial Current origin, while the low surface salinities indicate that this layer has originated farther South.

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THE GREAT BAHAMA BANK.
II. CALCIUM CARBONATE PRECIPITATION

By

C. L. SMITH

Bahamas Sponge Fishery Investigation Department

I. PRECIPITATION OF CALCIUM CARBONATE

The exact mechanism whereby calcium carbonate is precipitated from sea water in shallow tropical seas has attracted the attention of many workers but as yet has not been adequately explained.

The matrix of events is very involved and to present the reader with a coherent account the sequence may be divided into four stages, each merging gradually into the other.

1. It is well known that the surface water of the Atlantic Ocean is heavily supersaturated with calcium carbonate (Wattenberg, 1933). The free carbon dioxide at the surface of the ocean is in equilibrium with that of the atmosphere, and so the partial pressure of carbon dioxide is approximately equal to the atmospheric value.

2. Some of this ocean water is continuously moving in over the shallow, calcareous banks to the West of Andros Island forming part of the extensive Great Bahama Bank (Pt. I). On this bank the water is considerably concentrated by evaporation and all constituents of the water begin to increase proportionately to one another. The water is very shallow, however, and wind action stirs up the bottom mud which contains countless minute aragonite needles (Thorp, 1936). This suspension in the water provides suitable nuclei for the precipitation of calcium carbonate from the heavily supersaturated solution.

The removal of carbonate and calcium ions from the system leads to an increased hydrogen ion concentration and the equilibria

$$H_2O + CO_2 \rightleftharpoons H^+ + HCO_3' \quad \ldots\ldots (1)$$

$$HCO_3' \rightleftharpoons H^+ + CO_3'' \quad \ldots\ldots (2)$$

are displaced to the left. In consequence of this shift the partial pressure of carbon dioxide rises and the pH exponent falls. That this is so may be seen by recasting the equations in the form

$$CO_3'' + CO_2 + H_2O \rightleftharpoons 2HCO_3' \ldots\ldots\ldots\ldots (3)$$

and examining the respective equilibrium constants of all three; bearing in mind the expressions

$$\text{Carb. Alk.} = C_{HCO_3'} + 2C_{CO_3''} + C_{OH'} - C_{H^+}$$

$$\Sigma CO_2 = C_{CO_2} + C_{HCO_3'} + C_{CO_3''}.$$

3. Later this water reaches the shallow inshore area where conditions are most favorable for precipitation. Here the partial pressure of carbon dioxide rises to nearly twice that required for equilibrium with the atmosphere. At the same time the continued removal of calcium carbonate so far depresses the value of the ionic product $Ca^{++} \times CO_3''$ that it attains a minimum value and precipitation diminishes. The field data for the ionic product at this stage are considered to provide an upper limit for the solubility product of calcium carbonate in sea water under natural conditions.

4. In the previous stage the calcium carbonate in solution was approaching equilibrium but the water was heavily supersaturated with carbon dioxide and the pH exponent was low. This water in accordance with the general circulation over the bank moves back towards the open ocean. The carbon dioxide tension begins to fall owing to evasion to the atmosphere. This causes a shift of the equilibria shown in equations (1), (2) & (3) to the right and the pH exponent and carbonate ion content rise. Since the calcium content remains fairly constant the ionic product $Ca^{++} \times CO_3''$ increases and the water once more becomes supersaturated with calcium carbonate. Some precipitation of this excess undoubtedly occurs as the water moves off the bank, but as admixture with heavily supersaturated ocean water is beginning equilibrium can never be re-attained. Eventually this small water mass which has been followed on its journey across the bank is reabsorbed into the ocean.

Observations which may be used for checking the accuracy of the above hypothesis were made in April, October and December, 1939, the station positions being shown in Figure 52.

In the interests of simplicity the data for October will be presented in detail and the rest given en bloc as confirmatory evidence.

It is necessary to recapitulate briefly the main water movements on the bank in late September and early October. The distribution of the isohalines (Fig. 48 Pt. I) shows a marked westerly drift of highly saline water across the central part of the area with sharp salinity transition zones on the edge of the Florida Channel and at the northern end of Andros Island. The assumption that the greater part of

the fresh ocean water flowing in to replace the westerly drift comes from the northern part of the bank along the coast of the island has already been explained (Pt. I, p. 163). Similarly that eddy currents may occur on either side of the apex of the wedge of high salinity water was also discussed. With this in mind the stations worked in

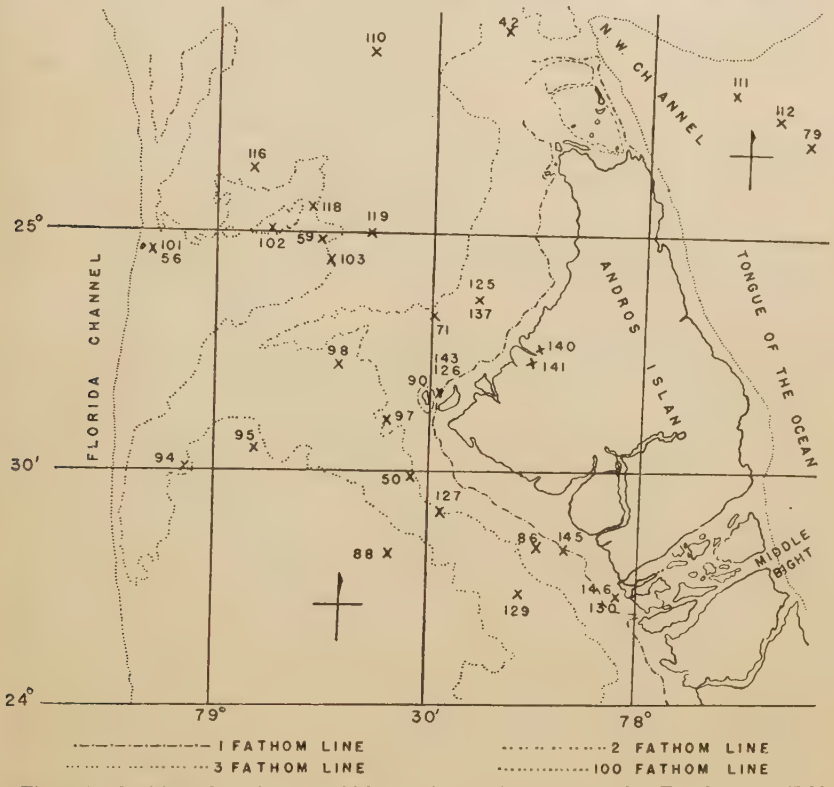

Figure 52. Position of stations at which complete analyses were made. For dates see Tables I, II and III.

October (Fig. 52) are able to show the main features of the whole cycle of changes taking place in the water while on the bank.

The observed data for temperature, chlorinity, titration alkali, calcium content and pH_w are shown in Table I, together with the values of the various quantities entering into the carbonic acid equilibrium (calculated from the tables of Buch et al (1932) and Buch (1933)).

For convenient interpretation this table is divided into four sections to correspond with the stages of the hypothesis previously out-

TABLE I

THE CYCLE OF CHANGES ACCOMPANYING PRECIPITATION OF CALCIUM CARBONATE
SAMPLES COLLECTED SEPTEMBER 29TH–OCTOBER 9TH, 1939

Station	*Temp.** °C.	*Cl.** °/₀₀	*Titrat.* Alk.* m.eq./l.	*Carb.+ Alk.* m.eq./l.	P_{CO_2}+ 10^{-4} atmos.	ΣCO_2+ m.mol/l.	C_{CO_2}+ m.mol/l. $\times 10^{-2}$	$C_{CO_3''}$+ m.mol/l.	$C_{Ca^{++}}$* m.mol/l.	$Ca^{++} \times CO_3''$ $\times 10^{-6}$	pH_w*	ΔCO_2 m.mols/l.
					I. Open Ocean Water							
111	30.0	20.17	2.511	2.36	2.5	1.98	0.68	0.38	11.25	4.28	8.28	
					II. Water Moving on to the Bank							
101	29.4	20.24	2.393	2.26	2.8	1.93	0.66	0.33	11.20	3.70	8.23	0.0
110	29.6	20.43	2.386	2.27	3.0	1.94	0.69	0.33	no obs.	—	8.21	−0.02
88	31.0	21.85	1.940	1.88	5.1	1.72	1.19	0.16	11.70	1.87	7.99	0.03
90	30.5	21.88	1.792	1.73	4.0	1.57	0.91	0.16	11.75	1.88	8.07	0.11
					III. Product of $Ca^{++} \times CO_3''$ Approaching a Minimum Value							
86	30.2	22.35	1.769	1.72	4.7	1.59	1.07	0.13	11.97	1.55	8.01	0.11
97	30.4	22.05	1.696	1.66	4.6	1.53	1.04	0.13	11.85	1.54	8.01	0.11
					IV. (a) Water Losing CO_2 as it Leaves the Bank. Northern Section							
98	30.4	22.78	1.663	1.61	4.2	1.47	0.91	0.14	12.00	1.68	8.04	0.18
103	29.2	22.37	1.716	1.66	3.0	1.47	0.68	0.19	11.97	2.27	8.16	0.20
102	29.0	22.20	1.803	1.72	2.6	1.50	0.59	0.22	11.85	2.61	8.22	0.20
					(b) Southern Section							
95	30.2	21.16	1.866	1.82	4.7	1.65	1.09	0.17	11.35	1.93	8.02	0.05
94	30.2	21.27	1.934	1.86	4.0	1.67	0.95	0.19	11.55	2.20	8.08	0.06

* Direct observation

+ Calculated from tables of Buch et al (1932) and Buch (1933).

lined. Each of these sections may be briefly examined to see how far the hypothesis is borne out in practice.

I. The open ocean water has a low partial pressure of carbon dioxide, which is probably a little lower than that of the atmosphere owing to loss by photosynthetic processes. The water is also heavily supersaturated with calcium carbonate. It may be noted that these observations for ocean water agree closely with those obtained at "Atlantis" and "Meteor" stations in adjacent waters (Rakestraw and H. P. Smith, 1937, Wattenberg 1933).

II. In this section the stations are arranged in order of distance from the ocean. The pH exponent, the product $Ca^{++} \times CO_3''$, total carbon dioxide and titration alkalinity are all decreasing owing to the precipitation of calcium carbonate. At the same time the partial pressure of carbon dioxide is rising rapidly. These changes are all clearly shown despite the increasing concentration of all constituents by evaporation.

III. This section contains two stations where the down grade processes of Section II are approaching equilibrium. The value of the product $Ca^{++} \times CO_3''$ has attained the minimal value found during the cycle and represents a maximal value for the solubility product of calcium carbonate. The water has now become heavily supersaturated with carbon dioxide, so that in the shallow water (2 to 3 metres) evasion to the atmosphere must be proceeding rapidly; equilibrium between carbon dioxide evasion and calcium carbonate precipitation is approached, the product $Ca^{++} \times CO_3''$ remaining more or less constant.

IV. When the water moves westward out of the relatively stagnant inshore area the conditions for calcium carbonate precipitation become less favorable. Loss of carbon dioxide to the air now becomes the dominant process. Stations 98, 103 and 102 illustrate this clearly for the chlorinity shows that only slight tidal admixture with ocean water has taken place up to this point. The partial pressure of carbon dioxide falls to that of the open ocean water, and the consequent displacement of the equilibrium has increased the carbonate ion content so that the water is again supersaturated with calcium carbonate. Precipitation of calcium carbonate must be still going on at this stage, but it is too slow to keep the ionic product constant. Stations 95 and 94 show the same process in action but owing to eddy currents in this locality they are not comparable in point of distance from the land with the more northerly stations.

The water moving westward toward the edge of the bank even in the northern section is being mixed by tidal action with some ocean

water of low salinity and high titration alkalinity. This may lead to a rising value of titration alkalinity at these stations. An approximate correction may be applied to the observed titration alkalinity results to compensate for this mixing. For example between stations 98 and 102 the chlorinity shows that the water has been mixed with 22% of ocean water (see Appendix). This should give a titration alkalinity value for the mixed water of 1.849 m. eq./l. whereas the observed value was 1.803 m. eq./litre, so that calcium carbonate is still being precipitated as the water moves away from the shore. The amount of deposition shown by applying this correction is probably too low as no account has been taken of concentration by evaporation which must still be going on to some extent.

The column headed ΔCO_2 in Table I provides indirect confirmation of the process of carbon dioxide evasion to the atmosphere accompanying the above reactions. It is derived by calculating the titration alkalinity (*A′) which would be found if open ocean water were concentrated to the observed salinity of the sample by evaporation only. The difference between this quantity (A′) and the titration alkalinity found by direct analysis (A) is a measure of the calcium removed from the water as calcium carbonate. This process has removed an equivalent quantity of carbonate ion, and reduced the total carbon dioxide content by a corresponding amount. In millimoles per litre this becomes $\frac{A' - A}{2}$.

The total carbon dioxide which would be present if evaporation were the only process, $\Sigma CO_2'$, is now calculated. However, some of the carbon dioxide $\left(\frac{A' - A}{2}\right)$ has been removed by precipitation of solid calcium carbonate. If these were the only processes occurring, the total carbon dioxide remaining would be given by $\Sigma CO_2' - \left(\frac{A' - A}{2}\right)$. Its value would be identical with the total carbon dioxide content, ΣCO_2 net, deduced directly from the observed titration alkalinity and pH exponent.

But, during the cycle it has been shown already that the pH exponent falls and the partial pressure of carbon dioxide, P_{CO_2}, rises above the atmospheric value. The resulting loss of carbon dioxide (ΔCO_2) by evasion from the water is thus *superimposed* on the loss as precipitated calcium carbonate. The total carbon dioxide remain-

*Primed quantities such as A′ refer to changes brought about by evaporation only.

ing, ΣCO_2 net, after calcium carbonate has been precipitated and gaseous carbon dioxide has been evaded is therefore

$$\Sigma CO_2 \text{ net} = \left[\Sigma CO_2' - \left(\frac{A' - A}{2}\right)\right] - \Delta CO_2$$

At station 97, $\frac{A' - A}{2} = 0.52$ m. mols. CO_2/l., $\Sigma CO_2'$ would have been 2.16 m. mols/l. and ΣCO_2 net is 1.53 m. mols/l. In consequence the carbon dioxide evaded, ΔCO_2, amounts to 0.11 m. mols/l.

The tabulated results show that there is no significant evasion of carbon dioxide (ΔCO_2) until the water has been on the bank some time, but, once a high partial pressure of carbon dioxide has been built up, the process of evasion to the atmosphere goes on apace. The maximum amount lost is found in Section IV where carbon dioxide evasion to the atmosphere has already been found to be the dominant process.

The above detailed description shows that in October 1939 the full observations made at twelve stations on the bank do not conflict with the general cycle outlined in the original hypothesis. The essential part of the data has now been presented and the remainder of this section will be devoted to a discussion of the confirmatory results.

Table II contains the data for a number of stations worked in April 1939, these unfortunately being the only ones for which complete analyses are available.

These observations when considered in conjunction with the known water movements at the time of sampling (Pt. I, Fig. 47) again confirm the applicability of the general theory. Observations have also been made during the winter months (Table III).

At this time the water movements are liable to rapid fluctuations in strength and direction owing to the variable winds. Therefore although the water movements may be known at the time of sampling, the previous history of the water cannot be inferred with the same certainty as in the summer season when the winds remain easterly over long periods. For example on December 15, 1939 the residual current was towards E.S.E. at Station 125 and on January 17, 1940 towards S.W. at the same place. In addition owing to the lower temperature and unsettled weather conditions the magnitude of all changes in the carbonic acid equilibrium is greatly reduced. Despite these adverse factors the data obtained fit into the general scheme with surprising consistency. All the stations (except No. 145) for which complete data are available show the carbonate equilibrium to be in that phase which the water movements would lead one to

TABLE II

THE CYCLE OF CHANGES ACCOMPANYING CALCIUM CARBONATE PRECIPITATION
SAMPLES COLLECTED APRIL 18TH–22ND, 1939

Station No.	T° C.*	Cl.* °/₀₀	Titrat.* Alk. m.eq./l.	Carb.+ Alk. m.eq./l.	P_{CO_2}+ 10^{-4} atmos.	ΣCO_2+ m.mol/l.	$C_{CO_3''}$+ m.mol/l.	$C_{Ca^{++}}$* m.mol/l.	$Ca^{++} \times CO_3''$ $\times 10^{-6}$	pH_w*	ΔCO_2 m.mol/l.
				I. Stage I. Ocean Water							
79	25.0	20.05	2.455	2.32	2.4	1.96	0.36	11.47	4.12	8.29	
				II. Water Moving on to the Bank							
42	25.8	20.08	2.440	2.31	2.4	1.95	0.36	11.17	4.02	8.29	0.0
50	25.7	22.00	2.045	1.96	3.2	1.74	0.22	12.07	2.66	8.11	0.09
				III. Product $Ca^{++} \times CO_3''$ Approaching a Minimum Value							
71	25.7	23.98	1.945	1.87	4.2	1.72	0.15	13.07	1.95	8.05	0.13
				IV. Water Losing CO_2 as it Leaves the Bank							
59	25.6	23.45	1.915	1.84	3.7	1.66	0.18	12.77	2.30	8.09	0.15
56	26.3	21.86	2.130	2.04	2.4	1.77	0.27	12.17	3.29	8.23	0.10

TABLE III

THE CYCLE OF CHANGES ACCOMPANYING PRECIPITATION OF CALCIUM CARBONATE
STATIONS MARKED ‡ JANUARY 17TH–19TH, 1940, OTHERS DECEMBER 4TH–14TH, 1939. VALUES OF ΔCO_2 TOO SMALL TO BE SIGNIFICANT. † AN ANOMALOUS VALUE. MAY BE DUE TO AN ERROR IN TITRATION ALKALINITY

Station No.	*T°C.**	*Cl.** °/₀₀	*Titrat.* Alk.* *m.eq./l.*	*Carb.+ Alk.* *m.eq./l.*	P_{CO_2}+ 10^{-4} *atmos.*	ΣCO_2+ *m.mol/l.*	$C_{CO_3''}$+ *m.mol/l.*	$C_{Ca^{++}}$* *m.mol/l.*	$Ca^{++} \times CO_3''$ $\times 10^{-6}$	pH_w*
				I. Open Ocean Water						
112	25.0	20.33	2.469	2.34	2.3	1.96	0.38	11.25	4.28	8.31
				II. Water Moving on to the Bank						
116	21.4	20.58	2.445	2.31	2.2	1.98	0.33	no obs.	—	8.30
118	21.4	20.37	2.401	2.27	2.4	1.96	0.31	no obs.	—	8.28
119	21.0	20.46	2.440	2.31	2.3	1.99	0.32	no obs.	—	8.29
125	21.3	20.77	2.330	2.23	3.0	1.98	0.25	11.50	2.88	8.18
126	22.1	20.78	2.254	2.17	3.6	1.95	0.22	11.47	2.52	8.14
‡*140*	23.9	23.41	2.582	2.44	2.5	2.11	0.33	13.12	4.32	8.28
‡*141*	20.4	21.75	2.531	2.44	4.3	2.21	0.23	12.20	2.81	8.08
				III. Product $Ca^{++} \times CO_3$ Approaching a Minimum Value						
‡*137*	20.9	20.92	2.236	2.18	4.6	2.00	0.18	11.60	2.08	8.03
‡*143*	20.2	21.30	2.170	2.11	4.6	1.94	0.17	11.75	2.00	8.02
				IV. Water Losing CO_2 as it Leaves the Bank						
‡*145*	22.0	20.16	1.896	1.84	4.0	1.70	0.14	11.27	1.58†	8.05
‡*146*	22.2	20.45	2.114	2.04	3.5	1.86	0.18	no obs.	—	8.11
127	21.4	21.17	2.252	2.17	3.6	1.95	0.22	11.60	2.56	8.12
129	21.7	20.10	2.019	1.95	3.3	1.76	0.19	10.80	2.06	8.14
130	22.0	18.41	1.978	1.91	3.3	1.74	0.17	10.12	1.72	8.12

expect. Station 145 is anomalous in that the product $Ca^{++} \times CO_3''$ is very low (1.58×10^{-6}) but an error of 0.04 m. eq./l. in the titration alkalinity determination would be sufficient to cause such a discrepancy. The minimum ionic product for the winter stations is of the order of 2.00×10^{-6} at 21° C. and 21.3 ‰ Cl (Stations 137, 143). The observations at stations where evasion of carbon dioxide is dominant, following the nearest approach to equilibrium (Stage IV), are complicated to some extent by dilution with land drainage, but the partial pressure of carbon dioxide does fall and there is a tendency for the product $Ca^{++} \times CO_3''$ to increase again.

The role of the many creeks and shallow lakes on the West coast of Andros as a factor in the concentration of the water has already been described. Stations 140, 141, were taken in a creek (Deep Creek) and a shallow lake respectively. It is interesting that they show the characteristic symptoms of water from which calcium carbonate is just beginning to be deposited (Stage II), despite their very high salinity.

In general the summer season is the most satisfactory period for making observations on the carbonate equilibria on the bank. The history of the water can be ascertained more accurately and there is more justification for regarding the circulation as a continuous system. It is intended to collect further and more extensive data to check against this theory of calcium carbonate deposition, when observations will be made on a more comprehensive scale with stations more evenly distributed. It will be evident that for clarity, the presentation of this theory and the data supporting it has had to be oversimplified. It is realized that the stages arbitrarily defined in this paper are all part of one continuous system and merge imperceptibly one into the other. Also when discussing the carbon dioxide deficiency shown at certain stations it is realized that removal of carbon dioxide by photosynthesis may enter into the value of this quantity, but this should not significantly affect the variation shown from station to station. Let it be accepted that such considerations have not passed unheeded, and whatever path we may choose to trace through the chain of events the essential picture remains unchanged and self consistent.

II. SEASONAL VARIATION IN CALCIUM CARBONATE PRECIPITATION

In Part I of this paper it was shown that the maximum annual variation of temperature of the water on these shallow banks is approximately 10° C. Such a temperature change will appreciably

change the solubility product for calcium carbonate in sea water. It is therefore to be expected that there will be a seasonal difference in the amount of calcium carbonate deposited by any given body of water while over these shallow banks.

TABLE IV

MAXIMUM CALCIUM CARBONATE PRECIPITATION FOUND ON VARIOUS CRUISES BASED ON TITRATION ALKALINITY

Date	*Station No.*	*Temp. °C.*	*Decrease in Excess Base m. eq./litre*	*$CaCO_3$ Deposited mgs. $CaCO_3$/litre*
22: 4: 39	71	25.7	0.992	49.6
4: 10: 39	98	30.4	1.182	59.1
13: 12: 39	129	21.7	0.442	22.1
19: 1: 40	143	20.2	0.433	21.6

In Table IV the titration alkalinity observed has been subtracted from that which should have been present if evaporation only had taken place, at those stations on each cruise where the maximal decrease in titration alkalinity had occurred. This quantity is regarded as equivalent to the amount of calcium carbonate precipitated. The seasonal variation is very marked, the deposition being 59 mgs. of $CaCO_3$/litre at 30° C. and 41.2 ‰ salinity and only 22 mgs./litre at 22° C. and 36.4 ‰ salinity. Without more detailed information as to the actual volume of water which flows on and off the bank at various times of the year it is not possible to compute the actual deposition of calcium carbonate on the bottom over a given period. The amount of total precipitation in the summer months is, however, quite probably double that taking place in the winter. Thorp (1936) has observed that the oolites from the bottom deposits on this bank show many laminae, which suggest frequent interruptions in their growth cycles. This accords rather closely with the idea that the amount of precipitation is greatly diminished every winter.

III. DISCUSSION

Full reviews of the theoretical considerations underlying the buffer mechanism of sea water and the solubility of calcium carbonate are to be found in Wattenberg (1933), Buch et al (1932) and Moberg et al (1934), and no further description is necessary here.

It is of interest, though, to consider the minimal values of the ionic product $Ca^{++} \times CO_3''$ recorded on the Great Bahama Bank. To

render them comparable with other values of the solubility product they may be corrected to a salinity of 36 ‰ by the coefficient found by Wattenberg (1933); for every increase of 1 ‰ salinity pK_{CaCO_3} changes by — 0.038. Thus at 30° C. and 36 ‰ salinity the ionic product is 1.27×10^{-6} (average of Stations 86 and 97). At 20° C. and 36 ‰ S. it is 1.77×10^{-6} (Station 143). This rate of change with temperature shows a value of — 0.014 for the logarithm of the temperature coefficient of K'_{CaCO_3} (log φ K'_{CaCO_3}), whereas Wattenberg derived a value of — 0.010 between 20° C. and 30° C.

To compare these values of the ionic product with the figures obtained by Wattenberg et al (1936) and Revelle and Fleming (1933) it is necessary to correct them all to standard salinity and temperature. This was effected by using the temperature and salinity coefficients found by Wattenberg, and the various values computed at 36 ‰ salinity are shown in Table V at the experimental temperatures.

TABLE V

VALUES OF K'_{CaCO_3} RECORDED IN THE LITERATURE AND USED IN TABLE VI. COMPUTED TO 36°/₀₀ S.

Authority	*Temp. °C.*	*Value of K'_{CaCO_3} at 36°/₀₀ S.*
Wattenberg and Timmermann 1936...	20	0.74×10^{-6}
	25	0.62×10^{-6}
	30	0.52×10^{-6}
Revelle and Fleming 1933.....	30	2.4×10^{-6}
This paper.....	20	1.77×10^{-6}
	30	1.27×10^{-6}

The application of these different sets of values to observed data is shown in Table VI, where the quantities $C_{Ca}{}^{++}$ and $C_{CO_3}{}''$ at Atlantic stations worked by the "Atlantis," the "Meteor," and the author are listed for the surface water. The "Atlantis" stations are located in the western Sargasso Sea, the "Meteor" stations in the western Central Atlantic, and the Providence Channel stations in a deep ocean channel between the Bahama Islands (Fig. 52).

The percentage saturation with calcium carbonate varies from roughly 100% to 800%, depending on which value of K'_{CaCO_3} is used and the temperature of the water.

The fact that the ionic product $Ca^{++} \times CO_3''$ has been shown to decrease to 1.27×10^{-6} (at 30° C. and 36 ‰ S.) under natural conditions shows that Revelle and Fleming's figure of 2.4×10^{-6} cannot represent the natural equilibrium. At least the true solubility product

TABLE VI

CALCULATED SATURATION VALUES OF CALCIUM CARBONATE, FROM RECORDED VALUES OF K'_{CaCO_3}, AT VARIOUS HYDROGRAPHIC STATIONS

Source of Analytical Data	*Temp. °C.*	*Ca^{++} m.mols/l.*	*CO_3'' m.mols/l.*	*% Saturation $CaCO_3$ using values of K'_{CaCO_3} from Wattenberg, etc. (1936)*	*Revelle, etc. (1933)*	*This paper*
*"Atlantis" Sta. No. 1465***						
Rakestraw & H. P. Smith (1937)	20.0	10.99*	0.31	460	113	192
*"Atlantis" Sta. No. 1467***						
Ibid. (1937)	20.7	10.95*	0.29	429	106	179
"Meteor" Sta. No. 287 (14° N., 46° W.)						
Wattenberg (1933)	25.0	10.64*	0.32	533	122	222
"Meteor" Sta. No. 291 (8° N., 52° W.)						
Ibid. (1933)	26.8	10.64*	0.30	541	123	228
Providence Channel No. 111						
This paper	30.0	11.25	0.38	823	178	337
Providence Channel No. 133						
Ibid.	23.7	11.50	0.33	619	136	245

* Ca^{++} values calculated from the relation $C_{Ca^{++}} = \frac{\text{Carb. Alk.}}{2} + 0.477\ Cl\ ‰$ (m. mols). Wattenberg (1933).

** Data re-computed to correct for the influence of borate.

should be equal to, or lower than 1.27×10^{-6} under such conditions, but the data is insufficient to show whether it can fall as low as Wattenberg's value of 0.52×10^{-6}. Such a solubility product would mean, however, that there is a tremendous degree of supersaturation with calcium carbonate in the tropical oceans in summer. On the same basis the minimum values so far recorded on the Bahama Bank represent approximately 250% saturation.

In the present year it is intended to extend the scope of this work in the Bahamas with the hope of securing more evidence as to the value of the true solubility product of calcium carbonate.

Drew (1914) made a study of the calcareous deposits on the West coast of Andros Island. From the evidence obtained he suggested that bacterial action on soluble calcium salts in the sea water was effecting the precipitation of calcium carbonate. This work was extended by Kellerman and Smith (1914) and Bavendamm (1932). They concluded that ammonifying bacteria were more active in calcium precipitation than Drew's *Bacterium calcis*. In addition Bavendamm failed to find large numbers of bacteria except in the mangrove swamps inland, and in consequence concluded these were the main areas of precipitation. Black (1933) came to a similar conclusion, although he pointed out that concentration by evaporation would cause some deposition over the central part of the bank. Lipman (1924) failed to find definite evidence for bacterial precipitation and concluded that such action could never be more than an accessory process accompanying physico-chemical precipitation.

The observations on the calcium carbonate equilibrium presented in this paper do not show any support for the bacterial precipitation theory. In the first place the bacterial hypothesis requires an initial increase in the pH exponent of the water due to the formation of ammonia. The actual data, however, show a marked decrease in the pH exponent as a dominant feature of Stage *I* in the cycle. The water does not become more alkaline until the main phase of calcium carbonate precipitation is over (Stage *IV*).

The data for stations 140 & 141 (Table III) are directly opposed to Bavendamm's and Black's suggestion that the inland swamps are the main areas of precipitation. These samples were taken about three miles inland in shallow lakes at low water, and show that very little calcium carbonate has been deposited. They do show, however, that rapid concentration by evaporation is taking place and very high salinities are attained even in the winter.

The fact that ocean sea water is supersaturated with calcium carbonate when it flows onto the bank renders the whole cycle of pre-

cipitation readily explicable on a physico-chemical basis. The physical features of the area and the semi-stagnant water conditions are all conducive to the deposition of the excess calcium carbonate. It is, of course, quite possible that some bacterial precipitation may be going on in mangrove swamps very rich in organic matter. This deposition, however, is believed to be very small compared with that produced by chemical precipitation over the hundreds of square miles of the Great Bahama Bank.

IV. METHODS

For a description of methods of sampling, temperature measurement, salinity and oxygen estimation see Part I.

Hydrogen ion concentration. The pH of the water was estimated colorimetrically using cresol red as indicator. The pH was estimated on board ship within a few hours of sampling, the sample bottle being kept tightly closed in the interim to prevent changes in the carbon dioxide content of the water. Palitzsch boric acid-borate buffers were used for making up the standard indicator tubes, which covered the range at pH 0.02 intervals. The following corrections were applied to the observed reading to obtain the pH in situ (pH_w) (Cooper 1933).

(I). Correction for difference in temperature between the water when collected and during the pH estimation

$$pH_w = pH_b + (a + \beta)\ (t_b - t_w).$$

(II). The negative correction for the salt error of cresol red at the salinity of the sample.

(III). The Walbum correction for the difference in the temperature at which the buffers were used and that at which they were calibrated. As the buffers were calibrated at 18° C. and used in the summer at temperatures as high as 30° C. this correction was considerable on such cruises (— 0.07 pH for ocean water).

The correction for difference in temperature between the buffers and the sea water did not apply as they had both attained the same temperature. All values of constants and factors for making these corrections have been taken from Buch (1937).

Titration Alkalinity, was determined by Wattenberg's (1930) method. All estimations were made in duplicate and those for reference stations in triplicate. From the average of a number of duplicate estimations the standard error is ± 0.003 m. eq./litre for any one observation.

Calcium. Gripenberg's method (1937) was used for estimating the calcium content of the water, 10 ml. of sea water filtered through

a Whatman No. 42 filter paper being taken for each estimation. The excess sodium oxalate was estimated by titration against standard potassium permanganate. The accuracy of the method was checked by multiple analyses on sea water alone and on sea water plus a known volume of standard calcium carbonate solution. The standard calcium solution was prepared by dissolving a known weight of pure calcium carbonate in pure concentrated hydrochloric acid. Table VII shows the calcium contents recorded by analysis compared with the theoretical amounts present.

TABLE VII

Analyses of Sea Water and Standard Calcium Solution. Standard Deviation from the Mean = ± 1.9 mgs. Ca/litre

Sea Water alone *Ca mgs./litre*	*Sea Water + 30 mgs. Ca./litre* *Ca mgs./litre*	*Standard Calcium Solution (diluted 50 times)* *Ca mgs./litre*	
446	478	By weight	By Analysis
442	474	600	602
442	474		
	476		

On one occasion when 46 analyses of 14 samples of sea water were made the standard deviation from the mean was found to be ± 4 mgs. Ca/litre for all observations. The calcium content of all samples was determined in duplicate and it is considered that the average results are subject to a maximum error of ± 3 mgs. Ca/litre.

Total carbon dioxide (ΣCO_2), C_{CO_3}'', PCO_2 have been computed from the titration alkalinity, pH_w, and temperature with the aid of the tables of Buch et al (1932) and Buch (1933). The influence of boric acid on the buffer mechanism of sea water has been corrected for.

V. ACKNOWLEDGEMENTS

I am greatly indebted to Dr. L. H. N. Cooper, of the Plymouth Marine Laboratory, England, for advice on methods of analysis and for his invaluable assistance with the theoretical considerations underlying the carbonic acid equilibria. I also wish to express my appreciation to the Administration of the Sterling Chemistry Laboratory, Yale University for their cooperation in providing library facilities. This work has been carried out as a part time research programme while engaged in Sponge Fishery conservation on behalf of the Government of the Bahama Islands, with the aid of a grant from the British Colonial Development Fund.

VI. SUMMARY

A hypothesis based on theoretical considerations is advanced showing the chemical changes which might be expected to accompany the precipitation of solid calcium carbonate from sea water. This hypothesis can be divided into four main stages:

1. Open ocean water is supersaturated with calcium carbonate before it flows on to the bank.
2. On the bank concentration by evaporation takes place and wind action causes seeding of the solution with aragonite needles from the bottom deposits. Calcium carbonate is precipitated and owing to a shift in the carbonic acid equilibria the carbon dioxide tension rises and the pH exponent falls.
3. In the shallow inshore water precipitation is more rapid and the ionic product $Ca^{++} \times CO_3''$ reaches a minimal value. This value is regarded as a maximal value for the solubility product constant of calcium carbonate in sea water.
4. As the water moves off the bank again precipitation diminishes and owing to evasion of carbon dioxide to the atmosphere the water once more becomes supersaturated with respect to calcium carbonate.

Observations of temperature, chlorinity, titration alkalinity, calcium content and pH made on the Bahama Bank during 1939 confirm this hypothesis very closely.

The maximal value of the solubility product of $CaCO_3$ observed under natural conditions is compared with experimental values recorded in the literature.

The observations presented in this paper show no support for the theory of calcium carbonate precipitation by bacterial agency, but suggest that the main deposition is effected by purely physico-chemical processes.

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APPENDIX

I am indebted to Dr. L. H. N. Cooper for the following formula for determining the percentage admixture of ocean water as the high salinity water moves westward off the bank.

Let $x =$ %age of water having a salinity a‰

$y =$ %age of water having a salinity b‰

Then as $x + y = 100$, the following equation may be derived:

$$\frac{x.a}{1000 - a} + \frac{(100 - x)b}{1000 - b} = \frac{100c}{1000 - c}$$

(where c represents the salinity of the mixed water).

As a, b and c are observed quantities, x and y may be found by substitution.

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